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Variational calculations for the ground state of lithium.

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VARIATIONAL CALCULATIONS FOR THE GROUND STATE OF LITHIUM

by

David Kenneth McKenzie

Submitted to the

Faculty of Graduate Studies and Research

through the Department of Physics

in partial fulfillment

of the requirements for the Degree of

Doctor of Philosophy

at the University of Windsor

Windsor, Ontario, Canada

May, 1991



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Abstract

A multiple basis set extension of the doubled basis set methods originally developed by Drake et al.⁵ for Hylleraas type calculations in two-electron systems is applied to the $1s^2 2s\ ^2S$ ground state of Li. An 1134 term basis set containing all sums of powers of the distance coordinates up to seven yields an improvement of two orders of magnitude in the accuracy of the best previous upper bound to the non-relativistic ground state energy, $-7.478\ 059\ 54\ \text{a.u.}$ ¹². The upper bound obtained is $-7.478\ 060\ 312\ \text{a.u.}$, with an extrapolated energy $-7.478\ 060\ 326\ (10)\ \text{a.u.}$. This is in agreement with a new semi-empirical estimate of this value which is approximately 10 microhartrees above published semi-empirical estimates of the non-relativistic ground state energy. New calculations of the relativistic and QED corrections are required to resolve the discrepancy. A value for the Fermi contact term of $2.9054\ (3)\ a_0^{-3}$ is calculated, compared with the experimental value of $2.9061(3)\ a_0^{-3}$.

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1. INTRODUCTION

The use of trial wavefunctions that depend explicitly on non-negative powers of the inter-electronic coordinates $r_{ij} = |\vec{r}_i - \vec{r}_j|$ in variational calculations was introduced by Hylleraas¹ in 1928 to study the helium atom. Shortly thereafter the use of such wavefunctions was extended to three-electron systems by James and Coolidge^{2,3}, who examined both the hydrogen molecule and the lithium atom ground state.

The importance of Hylleraas-type (Hy) wavefunctions in variational calculations to obtain significantly improved precision eigenvalues for few-electron systems was immediately apparent, and by the late 1950's, Pekeris⁴ obtained for the non-relativistic ground state energy of He a result accurate to 1 part in 10^{10} , exceeding experimental results of the day by nearly two orders of magnitude. Current day calculations for the non-relativistic ground state eigenvalue⁵ have reached a precision of 1 part in 10^{14} , and a few parts in 10^{17} to 10^{18} for excited states^{6,7}, allowing for high precision comparison of quantum electrodynamic (QED) and high-order relativistic effects with experimental results.

Unfortunately, however, high precision results for three-electron systems have proven to be much harder to achieve. Even ten years after Pekeris' precise He calculation, the best results available for the non-relativistic ground state energy of lithium (due to Larsson⁸) was only accurate to about 5 parts in 10^6 , and it is only within the past few years that calculations with accuracies approaching 1 part in 10^7 have been reported⁹⁻¹².

It is interesting to note that while progress in improving the accuracy of variational results for three-electron systems has been slow, over the past twenty years considerable success has attended the development of many-body perturbation theory (MBPT) methods and its application to these systems. For example, within

a few months of Larsson's result mentioned above, a calculation of the non-relativistic ground state energy using MBPT techniques ¹³ gave a result accurate to a few parts in 10^4 . By 1985, Lindgren ¹⁴ had improved this to only a few parts in 10^6 , rivaling the most accurate results available at the time. Similar accuracy has been recently achieved for the valence removal energy using a relativistic formulation of MBPT ¹⁵. The latter results were obtained as a part of an effort to extend the applicability of Lindgren's methods to the study of QED effects in high- Z three-electron ions ^{16, 17}. As a factor of Z^{-1} is introduced with each new order in MBPT, convergence improves as Z is increased. In addition, relativistic and QED effects are more pronounced for high- Z systems, and therefore more easily observed.

For two-electron systems, Drake ¹⁸ has remarked that at low Z , better results are obtained by solving the non-relativistic Schroedinger equation to high accuracy and then including relativistic effects by using perturbation theory. Furthermore, for systems with more than two electrons he notes that the lack of high precision non-relativistic eigenvalues and relativistic corrections obscures the analysis of QED effects. The case of the lithium ground state, where a number of authors ^{19 - 21, 23} have made estimates of the non-relativistic ground state energy (E_{nr}), provides a good example.

Scherr et al. obtained a value of -7.4780690 a.u. for the non-relativistic energy E_{nr} of the $1s^2 2s$ 2S ground state of Li by adopting Pekeris' high precision non-relativistic eigenvalue for Li II and adding an estimate for the first ionization potential. This estimate was made by applying perturbation theory to develop an expansion for successive ionization potentials along isoelectronic series and fitting the results to empirical data, after adjusting for mass polarization, relativistic and QED effects (Lamb shift). The adjustment was made by assuming that an atomic system with N electrons can be decomposed into N one-electron contributions and

Table 1.1

Bunge's Estimate ²⁰ of the Non-Relativistic Energy of the Ground State of the Lithium Atom

Ionization Potentials ^a :			First	43 487.150 (5) cm ⁻¹	
			Second	610 079.0 (1)	
			Third	987 660.1	
E_{expt}				-1 641 226.3 (2) cm ⁻¹ or	-7.477 977 (2) a.u.
Normal mass effect					.000 585 a.u.
$E_{\text{infinite nuclear mass}}$					-7.478 562 (2) a.u.
Corrections:	Breit interaction		-0.000 551 a.u.	^b	
	K-shell relativistic correction		-0.000 067	^c	
	Lamb shift		+0.000 106	^c	
	Mass polarization		+0.000 023	^d	
					-0.000 489 a.u.
$E_{\text{non-relativistic (empirical)}}$					-7.478 073 a.u.

a. C.E. Moore, *Ionization Potentials and Ionization Limits Derived from the Analysis of Optical Spectra*, Natl. Stand. Ref. Dat. Ser. 34 (U.S. GPO, Washington, D.C., 1970) (unpublished)

b. S. Fraga and J. Karwowski, *Tables of Hartree-Fock Atomic Data*, Technical Report (University of Alberta, Edmonton, Canada, 1974) (unpublished)

c. H. Hartmann and E. Clementi, Phys. Rev. **133**, (1964) A1295

d. S. S. Prasad and A. L. Stewart, Proc. Phys. Soc. London, **87**, (1966) 159

then applying Dirac one-electron theory, combined with the one-electron Lamb shift, and modified by nuclear shielding parameters. They further assumed that the relativistic contribution of a closed shell is a constant independent of the number of electrons in the closed shell.

Muszynska et al.²³ also made their estimate of E_{nr} , -7.478068 a.u., by adding to Pekeris' two-electron ion energy an estimate for the first ionization potential. In this case the estimate was obtained by making a relativistic adjustment to the experimental ionization energy by regarding this energy as that of a shielded Dirac electron.

Bunge's estimates of E_{nr} , -7.478073 a.u.²⁰ and $-7.478071(5)$ a.u.²¹ with the figure in brackets representing the estimated uncertainty in the last figure, are deduced in a different fashion. The second of these estimates was obtained by noting, first, that the difference between experimental and non-relativistic energies for several states²² ($1s^2 2p$; $1s^2 \text{Li}^+$; $(1s2s)^3\text{S Li}^+$; $(1s2p)^3\text{P Li}^+$) are all just about equal and close to -0.000490 a.u., and second, that the relativistic energy corrections for the $1s^2 nl$ energy states change smoothly when n is increased for given l . Together these suggest that the total relativistic, radiative and mass polarization corrections for the ground state as well will be very close to the same value (-0.000490 a.u.). In the earlier paper cited, Bunge "constructs" this value from published calculations of these corrections, and applies it to the sum of the experimentally observed first, second and third ionization energies for lithium to obtain his estimate for the non-relativistic ground state energy. To illustrate the sizes of the individual corrections involved, Bunge's construction is presented in Table 1.1..

All of these estimates of E_{nr} are significantly lower than the best published variational upper bound value, -7.47805953 a.u., due to King and Bergsbaken¹². Bunge's estimate of $-7.478071(5)$ a.u., which brackets all the other estimates, would

suggest that this result is at least 6 microhartrees and perhaps as much as 16 microhartrees too high. As King and Bergsbaken have remarked, it seems very unlikely that the correct value for E_{nr} can be this much lower. Based upon the convergence pattern of the energy components in their work, they believe that their value for E_{nr} is accurate to within 1 microhartree and therefore that the literature estimates are in error by almost the entire amount of the discrepancy. They acknowledge, however, that their results are not conclusive of this, merely suggestive.

In fact, a careful re-examination of Bunge's construction in Table 1.1 confirms their suspicion. The K-shell relativistic correction of Hartmann and Clementi already includes the correction for mass polarization. Eliminating this double count increases the magnitude of the Breit interaction from $(-0.000551 - 0.000067 =)$ -0.000618 a.u. to -0.000641 a.u., raising Bunge's estimate of E_{nr} to -7.478050 a.u.. Adopting recent higher precision calculated values for the second and third ionization potentials, the two-electron Lamb shift, and the mass polarization, a better estimate for E_{nr} is -7.478060 a.u., as shown in Table 1.2..

The tentative nature of the conclusion of King and Bergsbaken regarding the true value of E_{nr} is due to the impossibility of confidently extrapolating from their calculations a sufficiently precise estimate of E_{nr} . The difficulty lies in establishing a pattern of convergence as the basis set is enlarged which is clear enough to be usefully predictable.

This problem, which has affected all studies of the lithium ground state employing correlated variational basis sets over the past twenty-five years, is a result of the highly arbitrary manner in which new terms are selected for addition to the set of basis functions that will be used to compose the trial wavefunction. In virtually all cases, to keep the size of the basis set manageable and avoid troublesome integrals, highly selected terms are added to the basis set chosen for

Table 1.2

Revised Estimate of the Non-Relativistic Energy of the Ground State of the Lithium Atom

Ionization Potentials :	First ^a	43 487.150 (5) cm ⁻¹	
	Second ^e	610 078.526	
	Third ^f	987 661.008	
E_{expt}		-1 641 226.684 (5) cm ⁻¹ or	-7.477 979 a.u.
Normal mass effect			0.000 585 a.u.
$E_{\text{infinite nuclear mass}}$			-7.478 564 a.u.
Corrections:			
Breit interaction	-0.000 551	a.u. ^b	
K-shell relativistic correction	-0.000 090	a.u. ^c	
		-0.000 641	a.u.
Lamb shift ^e :			
from Li ⁺⁺ (1s)	15.930 cm ⁻¹		
incr. for Li ⁺ (1s ²)	8.938 cm ⁻¹		
	24.868 cm ⁻¹ or	+0.000 113	a.u.
Mass polarization		+0.000 024	a.u.
		-0.000 504	a.u.
$E_{\text{non-relativistic}}$ (empirical)			-7.478 060 a.u.

- a. C.E. Moore, *Ionization Potentials and Ionization Limits Derived from the Analysis of Optical Spectra*, Natl. Stand. Ref. Dat. Ser. 34 (U.S. GPO, Washington, D.C., 1970) (unpublished)
- b. S. Fraga and J. Karwowski, *Tables of Hartree-Fock Atomic Data*, Technical Report (University of Alberta, Edmonton, Canada, 1974) (unpublished)
- c. H. Hartmann and E. Clementi, *Phys. Rev.* **133**, (1964) A1295
- d. F. W. King, *Phys. Rev. A*, **34**, (1986) 4543
- e. G. W. F. Drake, *Can. J. Phys.*, **66**, (1988) 586
- f. W. R. Johnson and G. Soff, *At. Data Nucl. Data Tables*, **33**, (1985) 405

their impact in reducing E_{nr} . Attempting to discern a meaningful convergence pattern from the results of such a highly contrived sequence of calculations is very difficult, to say the least.

Thus one of the primary objectives of the present work, in addition to substantially improving the accuracy to which the ground state eigenvalue is known, is to introduce a more systematic selection method which will allow the eigenvalue to be extrapolated with more confidence from a series of calculations with basis sets of increasing size.

At the same time, it will be possible to calculate a number of matrix elements that will test the quality of the resulting variational wavefunction in different regions of configuration space where the optimization for energy may leave weaknesses. In particular the Fermi-contact interaction, which is known to be highly sensitive to the quality of the wavefunction at the origin, may be evaluated.

This matrix element is of particular interest since in the present study the wavefunction utilizes only one of the two linearly independent doublet spin functions, but with multiple sets of exponential parameters employed in the set of spatial basis orbitals. Larsson⁸, who conducted a fairly extensive convergence study of both the energy eigenvalue and the Fermi-contact term using only a single exponential set, found that adding the second spin function greatly improved the convergence of the contact term while having little impact upon the energy. He noted that to some extent the use of the second spin function was like introducing a second set of exponential parameters into the set of basis functions. This was, in fact, one of the original motivations for a study employing a basis set which explicitly makes use of more than one set of exponential parameters.

The desirability of such a study was further increased by the success of the doubled basis set method of Drake⁵, which introduced the use of a second set of exponential parameters to Hy basis sets in calculations along the helium

isoelectronic sequence. Although originally intended for studies of Rydberg states, where a natural physical interpretation could be attached to the two exponential sets, the method also proved highly successful in very significantly improving the accuracy achievable for even the ground state energy⁶. These results lent strong support to the hope that application of a doubled or multiple (in terms of the trios of exponential parameters) basis set technique to the study of the lithium ground state would be successful in accelerating convergence of the energy eigenvalue and obtaining more accurate wavefunctions than previously available.

2. HISTORICAL SURVEY

The earliest quantum-mechanical treatment of the lithium atom appears to have been due to Hargreaves²⁴ in 1929, who attempted a calculation using the original formulation of the self-consistent field (SCF) method of Hartree²⁵. However, several authors including Hargreaves himself noted deficiencies that rendered his results unsatisfactory^{26, 27}. In particular these calculations had neglected to account for exchange. The calculation was repeated a few years later by Fock and Petrashen²⁷, who reported a value of -7.21 a.u. for the ionic core and a valence removal energy of 0.1967 a.u., yielding a value of about -7.41 a.u. for the ground state energy of lithium.

In 1930 the first variational results (other than SCF calculations) appeared. Eckhart²⁸ performed calculations for the energy of several two- and three- electron configurations using simple hydrogen-like wavefunctions and used the results to obtain ionization potentials. For the configuration $(1s)^2 2s$ in particular, he used radial functions of the form

$$u(r) = \exp(-\alpha r)$$

$$v(r) = (1 - \gamma r) \exp(-\gamma r)$$

for the $1s$ and $2s$ orbitals respectively, with α and γ as the variationally determined parameters. While the resulting ionization potentials using these screened type wavefunctions for low- Z members of the Li isoelectronic sequence were accurate to within a few percent, the value for lithium itself was in error and was recalculated later by Wilson²⁶, who obtained the values of -7.3922 a.u. for the ground state energy and 0.1696 a.u. for the ionization potential using Eckhart's value of -7.2226 for the energy of the $(1s)^2$ ionic configuration.

In the same year, Guillemin and Zener²⁹ obtained a sharply improved value of -7.4183 a.u. by using a three parameter wave function. The additional parameter

(a) was in the function for the 2s orbital;

$$v(r) = (1 - ar) \exp(-\gamma r).$$

Zener³⁰ extended the use of such analytic wave functions to calculate atomic shielding constants for the remainder of the atoms in the same row (Be through Ne) of the periodic table, and noted that omitting the constant term in the 2s orbital function v has little effect upon the wavefunction (relatively speaking, the parameter a is much larger), particularly as Z is increased. This prompted Slater³¹ to suggest that the radial part of a one-electron wavefunction could be simply expressed as

$$r^{n^* - 1} \exp[-(Z - s)r / n^*],$$

i.e., the asymptotic form (at large r) for a hydrogen-like wavefunction with effective quantum number n^* subject to a screened nuclear charge $(Z - s)$. Slater did not determine the parameters n^* and s variationally, but set up simple *ad hoc* rules to obtain values that provided reasonable agreement with observations of total energy and size of atoms and ions over a broad range of atomic number. (For lithium, these parameters would be $n^* = 1$, $s = 0.3$ for the 1s orbitals and $n^* = 2$, $s = 1.7$ for the 2s orbital, so the exponential parameters would be 2.7 and 0.65 respectively for these orbitals. The approximate energies according to Slater's rules should be -7.50125 a.u. for the ground state energy and 0.21225 a.u. for the ionization potential.) Subsequently, Slater³² showed that it was still possible to make a 2s orbital function orthogonal to the 1s function without affecting the overall determinantal atomic wavefunction.

In 1933 Wilson variationally tested both Slater's simpler form for the 2s orbital radial wavefunction,

$$v(r) = r \exp(-\gamma r)$$

and a three-parameter generalization

$$v(r) = ar \exp(-\gamma r) - \exp(-\xi r)$$

of the two-parameter function used by Guillemin and Zener. As expected, use of the simpler function only slightly raised the energy eigenvalue from the value of Guillemin and Zener to -7.4179 a.u. (an increase of 0.0004 a.u.), while the more flexible form improved the value by only slightly more, reducing it to -7.4192 a.u.. When combined with Eckhart's energy for $(1s)^2 \text{Li}^+$, this leads to a value of 0.1965 a.u. for the ionization potential. It was found that the optimum values of the variational constants could be conveniently expressed in terms of screening constants as

$$\alpha = Z - \sigma_1$$

for the $1s$ orbitals, and

$$\gamma = (Z - \sigma_2) / 2$$

$$\gamma' = (Z - \sigma'_2) / 2$$

$$a = (Z - \sigma_1) / 2$$

for the $2s$ orbital. The optimum values for these parameters were found to be associated with the screening constants $\sigma_1 = 0.31$, $\sigma_2 = 1.67$ and $\sigma'_2 = 0$, so that the optimum non-linear parameters α , γ , and γ' for the ground state of lithium were 2.69 , 0.67 , and 1.5 respectively. The corresponding optimum values for the simpler functions considered were very close to these. In addition, values of the screening constants proved to be essentially independent of the nuclear charge. Wilson also applied the variational principle to calculate the lowest P state, using a $2p$ radial wavefunction of the form

$$v(r) = (b \exp(-\mu r) + \exp(-\nu r)) r \cos \theta.$$

When optimized, the first term was found to vanish, leaving a wavefunction of the same form as previously used by Eckhart and giving an energy of -7.35039 a.u., which in conjunction with the calculated ground state energy yields a value for the resonance potential of 0.06876 a.u. that is only about 12 percent higher than the

experimentally observed value.

Thus by the early 1930's a variety of simple analytic wavefunctions had been used as variational test functions for the ground state and resonance level of lithium, achieving an accuracy of about 5×10^{-3} a.u. (approximately one-tenth of an electron volt) for the ionization and resonance potentials, but about an order of magnitude worse for the actual energy levels from which these potentials were derived. While these results were certainly regarded as very encouraging, the accuracy obtained by Hylleraas¹ in 1929 for the ground state energy of helium with a simple six-term wavefunction that included explicitly the interelectronic coordinate r_{12} was about two orders of magnitude better. Indeed, Wilson would have liked to introduce such interaction factors in his three-electron calculations, but as he points out, this "enormously complicates the problem in the case of lithium and so was not regarded as practicable."³³

The "complications" were first addressed for the case of lithium by James and Coolidge³ in 1936. As mentioned earlier, these authors had previously applied Hylleraas-type coordinates to the study of the hydrogen molecule² and were at the same time applying them to the study of the $1s2s\ ^1S$ state of helium³⁴. In the case of lithium, they were concerned about the reliability of the potentials discussed above, which appeared to be calculable to an accuracy more than an order of magnitude better than the calculated energy levels of which they were the difference. To address this concern, they set out using three different approaches to examine what effects improvements in the wavefunctions would have for both the bound states and the ionization potential.

First, they tried to improve the flexibility of the separate orbital functions over those of Wilson. As it was already known from studies of helium that the simple product of hydrogen-like functions such as those used by Wilson was completely inadequate to represent the core orbitals, they focused first on improving

the representation of the 2s orbital. They found, however, that even by using a considerably more elaborate function, i.e.

$$v(r) = c_1 r \exp(-0.665r) - c_2 \exp(-1.25r) + c_3 \exp(-1.5r) + c_4 \exp(-1.75r),$$

that no significant (less than 0.0001 a.u.) improvement was obtained.

Second, to try to improve the core representation, they abandoned the notion of a separate-orbital product function ($u(r_1)u(r_2)$) for the core and constructed a single function ($u(r_1, r_2)$) to represent the inner shell. They tried several functions representing progressively better approximations to the true ion function, starting with the simple exponential, $\exp[-3(r_1 + r_2)]$, and then adding a factor with a series of terms which grew to include $(r_1 + r_2)$, $(r_1^2 + r_2^2)$, and finally explicitly introducing r_{12} and r_{12}^2 . For each of these they computed the ion energy and then calculated the atomic ground state energy using two different 2s orbital functions, the simple Slater-type orbital (STO) and the slightly more complex function introduced by Guillemin and Zener, for comparison purposes. As long as the functions weren't too bad, they found that the ionization energy was almost independent of the inner shell representation and that the changes that did occur when the inner core representation was altered were almost independent of the function used to represent the valence orbital. Thus, provided that the inner core and valence representations are reasonably good, one can optimize either representation independently, with the ionization energy depending principally upon the quality of the valence orbital representation. They also tried calculating the atomic ground state energy in two different ways, first by separately optimizing the ionic core energy and then adding the valence orbital function, and second by optimizing some of the core coefficients (using the same valence function) within the calculation of the atomic energy, and found negligible difference (less than 0.00002 a.u.). On the basis of this computational experiment, they concluded not only that Wilson's (and Eckhart's) approach of taking the difference between the ion and

atom energies calculated with the same core to determine the ionization potential was reasonable, but that even solving the two variational problems separately and taking the difference between the eigenvalues should prove reliable.

The best value for the ground state energy of lithium obtained in this part of the James and Coolidge study was -7.47265 a.u., a remarkable improvement over previous results, especially in view of the simplicity of the wavefunctions used – a six-term core and a single term valence orbital function. The corresponding ionic core energy obtained by James and Coolidge was -7.27888 a.u., leading to an ionization potential of 0.19719 a.u., about 0.0014 a.u. too small. The optimum value found for the exponential parameter for both of the core orbitals was 2.69 , very close to the value obtained by previous workers when the same function was used for both $1s$ orbitals. For the valence orbital terms with two different exponential parameters were used, 0.65 and 1.5 , as in Wilson's study.

The third aspect of their examination was the inclusion of polarization effects between the core and the valence electron, which they attempted to incorporate by abandoning completely the concept of separate orbitals and constructing the wavefunction for the atomic state with terms including the interelectronic coordinates r_{13} and r_{23} to allow for correlation between the valence orbital and the core, as well as terms with r_{12} and r_{12}^2 which allowed for correlation effects within the core. With a ten term wavefunction, a ground state energy of -7.47607 a.u. was obtained. Thus even the improvement due to allowing for core–valence orbital correlation effects was an order of magnitude greater than the improvements that previous researchers had been able to obtain by using separated–orbital models. James and Coolidge also estimated the convergence limit that seemed possible if higher order terms aimed at improving the description of polarization effects were to be included. This limit was -7.47796 ± 0.00026 a.u., and the estimated increment possible, 0.00188 ± 0.00026 was very close to the energy difference required to bring

the best ion core energy into agreement with experiment. They concluded that "to a satisfactory degree of approximation, the core function retains its identity even in the correct, nonseparable atomic function".

In their final three-electron calculations, as they had already established that the use of a slightly less than optimum core should be acceptable, they used the value 3.0 for the exponential parameter and estimated that this raised the energy value calculated by less than 0.0005 a.u..

Although we shall defer the details of its discussion until later, the critical computational element in James' and Coolidge's work is the calculation of the radial integrals

$$I(i,j,k,l,m,n;\alpha,\beta,\gamma) = \int d^3v \, r_1^i r_2^j r_3^k r_{23}^l r_{31}^m r_{12}^n \exp(-\alpha r_1 - \beta r_2 - \gamma r_3) .$$

In essence this integral is evaluated by expanding the powers of the interelectronic coordinates r_{ij} in the usual manner in terms of series of Legendre functions. These combined series terminate after a finite number of terms except in the case where all three powers l , m and n of the interelectronic coordinates are odd, in which case an infinite series is involved. James and Coolidge side-stepped this problem by including in their wavefunction only terms which contained a single non-zero power for one of the three interelectronic coordinates, thereby avoiding the occurrence of any of the troublesome integrals. This was not a serious limitation in their study as the final wavefunctions tested contained very few terms in any case, and not many terms were required to account for correlation effects. For subsequent researchers using Hylleraas-type coordinates, however, this integral would remain a key hurdle in the path to refinement of the James and Coolidge results.

The next major step in this regard would not come for three decades, after renewed interest had developed in calculations for the lithium ground state and the computing technology to make larger scale calculations feasible began to become

accessible to researchers.

The renewal of interest in the lithium ground state was focused largely upon calculations of the hyperfine structure, and these in turn were driven by efforts to improve the applicability of separate-orbital models. Even though these had been clearly established to be inferior to the nonseparable Hylleraas-type orbital models in the cases of helium and lithium, there was simply no alternative for more complex systems, and even for these simple systems the results of the separate orbital models tended to improve as one progressed to higher values of Z along the isoelectronic sequences.

The catalyst for this renewal seems to have been Slater's observation in 1951 that there must be solutions of the Hartree-Fock (HF) equations in which electrons of different spin are described by significantly different one-electron operators³⁵. One author to pursue this idea was Nesbet³⁶, who in 1955 challenged the usual Hartree-Fock assumption that all spin orbitals which have the same quantum numbers n and l , but different values of m_l and m_s , share a common radial part of the spatial orbital. The "unrestricted Hartree-Fock method" (UHF) suggested by Nesbet allowed different orbital functions for spin-orbitals with different values of m_s . The following year Pratt³⁷ predicted that using this model there would be a non-zero contribution to the hyperfine splitting of the $1s^2 2s\ ^2S$ ground state of lithium due to a small difference in the exchange contributions to the electron spin density at the nucleus between the $2s$ valence orbital and the two slightly differing core orbitals (distinguished as $1s$ and $1s'$). This prediction of a core "exchange" polarization prompted many calculations of the Fermi-contact term, responsible for the hyperfine splitting of this state, using a number of variants of the original unrestricted Hartree-Fock model and other separate-orbital models³⁸ in an effort to close the wide gap between the conventional Hartree-Fock value³⁹ of $2.095\ a_0^{-3}$ and the experimental value⁴⁰ of $2.906\ a_0^{-3}$.

Table 2.1

Selected results from self-consistent-field models for the $(1s^2)2s\ ^2S$ state of Li

Ref.	Author(s)/ Date	Method	Comments	- Energy (a.u.)	$\langle 4\pi \delta(\vec{r}_i) \sigma_{z_i} \rangle$ (a_0^{-3})
39	Sachs 1960	HF	single determinant	7.432 727	2.095
	" "	UHF		7.432 751	2.825
42	Lunell 1968	UHF	projected after var.		2.345
	" "	UHF	complete spin function	7.432 791	2.753
41	Goddard 1967	UHF	$\Psi = A_1\psi_1 + A_2\psi_2$ projection before var. fixes ratio $A_2/A_1 = -1/3$	7.432 813	3.020
42	Lunell 1968	UHF	ψ_1 only	7.447 529	2.582
		UHF	$\Psi = A_1\psi_1 + A_2\psi_2$ projection after var. determines ratio $A_2/A_1 = -0.00253$	7.447 536	2.846

Although Pratt highlighted the fact that the general form for a wavefunction of doublet symmetry for a three-electron system is

$$\Psi = A_1\psi_1 + A_2\psi_2 \quad (1)$$

where the A 's are the linear variational coefficients and the ψ 's are the two linearly independent doublet wavefunctions

$$\psi_1 = \mathcal{A}\{ u_{1s}u_{1s'}v_{2s} (\alpha\beta\alpha - \beta\alpha\alpha) \} \quad (2)$$

$$\psi_2 = \mathcal{A}\{ u_{1s}u_{1s'}v_{2s} (2\alpha\alpha\beta - \alpha\beta\alpha - \beta\alpha\alpha) \} \quad (3)$$

and \mathcal{A} represents the three particle antisymmetrizer, he believed that a much simpler form should be adequate to yield satisfactory computational results. As he anticipated that the $1s$ and $1s'$ orbital functions should be only very slightly different, he expected the two determinantal wavefunctions $\mathcal{A}\{ u_{1s}\alpha u_{1s'}\beta v_{2s}\alpha \}$ and $\mathcal{A}\{ u_{1s}\beta u_{1s'}\alpha v_{2s}\alpha \}$ should be nearly degenerate with each other. The omission of one of these two determinants should then only slightly increase the value of the energy calculated, so in that sense the use of only a single determinantal wavefunction should yield good computational results, even though it would introduce a small admixture of 4S symmetry. This did not prove to be true, and a number of alternative approaches based upon either the use of more than a single determinant in constructing the wavefunction to permit the correct symmetry to be obtained or projecting out the quartet components (either before or after optimizing the variational wavefunction), were required before a reasonable value could be obtained for the Fermi-contact term using the unrestricted HF approach. A few selected examples of results from these models are included in Table 2.1.

Sachs' ³⁹ single-determinant HF and UHF calculations, for example, show a dramatic improvement in the value of the Fermi contact term (although not in the energy) when the restriction to a common radial orbital function for the two core electrons is lifted. Sachs was also quick to point out that if one attempts to restore the correct symmetry to the computed UHF wavefunction by projecting out the

quartet component, a much poorer value is obtained.

Self-consistent-field calculations by Goddard and by Lunell demonstrate the importance of ensuring that the correct symmetry is present from the outset of the variational calculation.

In the first of a series of three papers, Goddard⁴¹ developed a set of projection operators, each of which yields an eigenfunction of \hat{S}^2 that satisfies the Pauli exclusion principle when it acts upon a function of the spatial and spin coordinates of N electrons. In the second paper he showed how these operators could be used to form a set of coupled integro-differential equations that could be solved in a self-consistent approach similar to the normal Hartree-Fock method, and in the third he applied the method to the ground state of lithium. The important characteristic of the method in the present context (cf. eq. (1)) is that it provides a fixed ratio of the components ψ_1 and ψ_2 , which are antisymmetrized products of the spatial orbitals with the two linearly independent doublet spin functions with $m_s = 1/2$,

$$\chi_1 = \alpha\beta\alpha - \beta\alpha\alpha,$$

$$\text{and } \chi_2 = 2\alpha\alpha\beta - \alpha\beta\alpha - \beta\alpha\alpha.$$

Lunell⁴² opted for a more straightforward modification of the normal UHF methodology when he used the notion of a generalized spin-orbital,

$$\phi(r_i)[\alpha(i) + A'_i\beta(i)],$$

where A' is a coefficient to be determined variationally, to form his Slater determinantal wavefunction. When the doublet component of this wavefunction is projected out, it can be reduced to the form given in equation (1), with only two variational coefficients instead of the three A'_i coefficients introduced with the three generalized orbitals. Lunell was thus able to perform separate calculations for the lithium ground state including the effect of both spin functions χ_1 and χ_2 , or only using χ_1 .

While both Goddard's and Lunell's wavefunctions improve the value for the Fermi contact term over that obtained with Sachs' projected wavefunction, the energy eigenvalues obtained by Lunell were significantly lower. The values for the Fermi contact term, however, show the importance of including some measure of the triplet-core doublet wavefunction χ_2 . Lunell's calculation, which utilized both doublet spin functions and allowed A_1 and A_2 to be determined variationally, left the energy essentially unchanged from the value obtained with only the singlet-core doublet wavefunction, but at 2.846 a_0^{-3} , gave the best value for the Fermi contact term, within 2.1 percent of the experimental value.

To further underscore the importance of including both doublet spin functions, Lunell repeated the UHF calculation of Sachs using the same radial orbitals but including the complete spin function, again with little impact upon the energy value, but a remarkable improvement in the value of the Fermi contact term.

While the impact of spin symmetry slowly became clear in self-consistent-field calculations on the lithium ground state, the central idea of the unrestricted scheme was also being explored in straightforward variational calculations using analytic wavefunctions.

The "open-shell" idea of differing core 1s orbitals was applied in 1957 by Burke and Mulligan⁴³ to a variational calculation of the ground states for the lithium isoelectronic sequence from Li to F^{6+} using a wave function of the form specified in equations (1) to (3) with radial functions u and v of the form

$$u_1(r_1) = \exp(-\alpha r_1), \quad u_2(r_2) = \exp(-\beta r_2), \quad v(r_3) = r_3 \exp(-\gamma r_3).$$

The optimum values of $\alpha = 3.3$, $\beta = 2.065$ and $\gamma = 0.642$ yielded an energy for the ground state of lithium of -7.44365 a.u. , a reduction of some 0.02575 a.u. over the "closed configuration" with $\alpha = \beta = 2.668$ and $\gamma = 0.630$ considered by Wilson some twenty-four years earlier, and in substantial agreement with the best variants of the Hartree-Fock method. A particularly interesting result of this work was the

observation that the relative importance of the second spin function increases with Z , with the ratio $|A_1/A_2|$ increasing from 0.64 percent for Li to 3.55 percent for F^{6+} . This agrees reasonably well with the corresponding value (0.25 percent) obtained much later by Lunell in his s.c.f. calculation⁴², and is far lower than the value (1/3) obtained by Goddard in his more restricted projection approach to the s.c.f. method. In addition, open-shell calculations using only the two-determinant function ψ_1 , a common approach among the UHF methodologies, would be expected to yield less accurate results than comparable calculations using both spin functions, and this would be true even more so at higher Z values where one normally expects better results from separated-orbital models. This behaviour was observed later by Nesbet.

Very similar calculations to those of Burke and Mulligan were undertaken independently by Brigman, Matsen et al.⁴⁵, using only ψ_1 as they had also discovered only slight improvement in the energy eigenvalue when the second antisymmetrized function ψ_2 was included. In 1961 Ritter, Pauncz and Appel⁴⁶, who used an expansion in generalized Laguerre functions to form a slightly more complex 2s orbital function which in particular was non-vanishing at the origin unlike the 2s STO (and also only included the first antisymmetrized function ψ_1). This wavefunction produced a sharp improvement in the ground state energy, to -7.4450 atomic units. Berggren and Wood⁵⁰ later calculated a value of $2.802 a_0^{-3}$ for the Fermi contact term using this wavefunction. Lunell⁴² would subsequently reexamine this calculation and conclude that it was a fortuitously good result occasioned by too short an expansion of Laguerre functions for the 2s orbital. With a slightly longer expansion he obtained the value $2.70 a_0^{-3}$, and the value deteriorated further as the expansion was lengthened. With ψ_2 included, however, Lunell found a corresponding value of $2.98 a_0^{-3}$ for the contact term, with convergence improving with the length of the expansion.

Ritter et al. also calculated the energies and ionization energies of the first four $(1s)^2 ns \ ^2S_{1/2}$ states for several members of the lithium isoelectronic sequence.

A much more elaborate study based upon superposition of configurations was undertaken by Weiss⁴⁷ in 1961, who examined two-, three-, and four-electron systems. Weiss began his study of the ground state of lithium by constructing a representation for the $1s^2 \ ^1S \text{ Li}^+$ ion core, and then used the same set of configurations (represented by Slater-type orbitals) multiplied by a new 2s orbital to form a properly antisymmetrized 35 term wavefunction. This wavefunction was then optimized variationally, but retaining the best exponential parameters that had been determined previously for the ionic core. To this were added ten more terms in two stages. First, six terms were added to help account for correlation with the core. To this point the two determinant wave-function was of the form ψ_1 . Four further terms were then included to admit some 3S core representation, mixing in the second function ψ_2 . The resulting energy eigenvalue for the final 45 term wavefunction, -7.47710 a.u., was the first to improve upon James' and Coolidge's result.

Weiss' intent in this work had been to see how well one could do using the configuration interaction [CI] approach with the computing equipment available. He concluded that "trying to obtain very accurate wavefunctions by configuration interaction rapidly becomes a case of hopelessly diminishing returns ... If something approaching Hylleraas or Pekeris type accuracy is desired for systems with more than two electrons, one will have to go to outrageously long expansions, probably too long for present day equipment."⁴⁸

Weiss did see the CI approach as being valuable for obtaining useful wavefunctions for other matrix elements than the energy and in 1963, together with Martin, used his 35-, 41- and 45-term wavefunctions to calculate the Fermi contact term⁴⁹. The 35-term function, which has only a nodeless Slater-type 2s orbital,

Table 2.2

Results of analytic variational calculations for the $(1s^2)2s\ ^2S$ state of Li

Author(s)/Date		Comments		-E (a. u.)	$\langle 4\pi \delta(\vec{r}_i) \sigma_{z_i} \rangle$ (a_0^{-3})
Wilson	1933	STO	single determinant	7.417 9	
		STO	4 parameter function	7.419 2	
Burke &	1958	$A_1\psi_1 + A_2\psi_2$	closed-shell STO's	7.417 90	
Mulligan			open-shell STO's	7.443 65	3.038 ^c
Hurst et al.	1958	ψ_1 only	closed-shell STO's	7.417 92	2.093 ^a
			open-shell STO's	7.443 6	3.772 ^a
Silverman	1963		private communication to Martin & Weiss ^a	7.417 95	3.233 ^a
Ritter et al.	1961	ψ_1 only	open-shell, STO's for core, Laguerre exp. $2s, \phi_{2s}(0) \neq 0$	7.445 0	2.802 ^b
Lunell	1968	ψ_1 only	Laguerre expansion	7.446 6	2.70
		$A_1\psi_1 + A_2\psi_2$	" "	7.446 6	2.98
Berggren & Wood	1963	ψ_1 only	closed-shell, r_{ij} core	7.474 76	2.648
		"	closed-shell, r_{ij} valence	7.476 06	2.828
			" incl. 1S coupled doublets	7.476 30	2.872
		$A_1\psi_1 + A_2\psi_2$	open-shell "	7.476 31	2.883
Burke	1963	ψ_1 only	Hy	7.476 95 ^d	
Weiss	1961	STO	35 term CI	7.474 02	3.989
			41 term CI	7.476 22	2.580
			55 term CI	7.477 10	2.595

a. Fermi contact term calculated by Martin & Weiss (1963) (Ref. 49)

b. " " " " " Berggren & Wood (1963)

c. " " " " " Kerwin & Burke (1962) (Ref. 44)

d. Corrected value calculated by Larsson & Burke (1968)

gave a very bad value, 3.989 a_0^{-3} , but even the other two functions with a more flexible valence representation and better able to account for core-valence orbital correlation gave results still lower than the experimental value by more than fifteen percent.

At about this time the first new calculations following the approach of James and Coolidge by introducing Hylleraas-type wavefunctions for the study of the lithium ground state began to appear.

Berggren and Wood⁵⁰ used the method to calculate the Fermi-contact term as well as the energy for a number of configurations only slightly more complicated than those used by James and Coolidge. Starting, in fact, from the same eight term separate-shell type wavefunction (which included powers of r_{12} to allow for correlation within the core) that had been employed by James and Coolidge, they added alternately powers of r_{23} and r_{13} up to the third, improving the ability to account for polarization of the core by the valence orbital.

Their results were interesting from a number of perspectives. First, even excluding terms that explicitly allowed for core-valence correlation, a reasonably good (in light of all prior calculations) value was obtained for the ground state energy (-7.47473 a.u.) and the Fermi contact term (2.648 a_0^{-3}) was improved over the value of Ritter et al.. By including a single term each employing r_{23} and r_{13} (i.e. the James and Coolidge form) the ground state energy was improved to -7.47606 a.u. and the Fermi contact term was found to be 2.828 a_0^{-3} , within 2.7 percent of the experimental value. Their best results, obtained with a 14 term function, were -7.47631 a.u. for the energy and 2.883 a_0^{-3} for the Fermi contact term. These results were obtained by allowing the symmetry between the two core orbitals to be broken by not requiring the linear coefficients to be the same for terms differing only by the interchange of coordinates 1 and 2 (eg. r_1 and r_2 or r_1^2 and r_2^2). They did, however, retain the use of a single common exponential parameter for the

1s core orbitals, so their test of the open-shell concept was rather limited.

Enforcing the symmetry constraint restricted the ground state wavefunction to the form ψ_1 , while the relaxed condition which introduced both singlet core doublet terms and quartet terms had an almost negligible effect upon the calculated values for energy, but improved the Fermi contact term value slightly.

In 1963, Burke⁵¹ also tried to extend the James and Coolidge results with a 13 term wavefunction, obtaining a ground state energy of -7.47695 atomic units. Although Burke had intended to employ a wavefunction of the form given by equation (1), he inadvertently restricted the functional form of the spatial orbitals to be symmetric with respect to the interchange of coordinates 1 and 2, thereby reducing his wavefunction to the form ψ_1 . Without this restriction his results would have matched the 45 term CI result of Weiss for the ground state energy⁵².

While an open-shell approach had proven to be an essential ingredient in improving the results obtainable for the lithium ground state with the Hartree-Fock method and with simple variational separated-orbital models employing superposition of configurations, the results of the variational calculations using Hylleraas type nonseparable orbitals suggested that the more direct method of accounting for correlation effects by including powers of the interelectronic coordinates in the wavefunction might be adequate even for studies of the hyperfine structure. Up to then, such wavefunctions had contained terms which individually had involved at most one such coordinate, r_{12} , r_{13} or r_{23} , and then at most to the second power. To handle effectively more complex wavefunctions of this type would require a computationally useful generalization of the cosine law for arbitrary powers of the coordinates r_{ij} and a reasonably efficient algorithm for the all-odd- r_{ij} -power integral mentioned earlier. The latter was addressed by Öhrn and Nordling⁵³ in 1963, while the former was treated by Sack⁵⁴ in 1964, who provided an expansion of r_{ij} to an arbitrary power in terms of hypergeometric

functions, and later by Perkins⁵⁵, who considered only integral powers of r_{ij} .

A dramatic improvement occurred in the values of both the ground state energy of lithium and the Fermi contact term when the new algorithms were applied by Larsson⁸ in 1968 in a detailed study using more complex Hylleraas type wavefunctions. In light of the erratic results of previous calculations of the Fermi contact term, Larsson presented results for every step in the expansion of his basis set as it increased to include 60 different spatial orbital terms. For each step he also displayed the results utilizing only one doublet spin function

$$\chi_1 = \alpha\beta\alpha - \beta\alpha\alpha$$

or both χ_1 and the second linearly independent doublet spin function

$$\chi_2 = 2\alpha\alpha\beta - \alpha\beta\alpha - \beta\alpha\alpha$$

with different variationally determined coefficients.

Larsson's calculation is of the closed-shell variety. The core orbital exponential parameters were chosen to be equal and when roughly optimized for a nine term wavefunction to the value $\alpha = \beta = 2.76$ with the valence orbital exponential parameter $\gamma = 0.65$, they remained close to the corresponding values for previous closed-shell calculations with Slater type orbitals. As the antisymmetrized product of a spatial orbital symmetric in coordinates 1 and 2 with χ_2 (also symmetric with respect to these coordinates) vanishes, only 40 of the 60 spatial terms considered could be used with the second spin function.

Larsson⁵² points out that only one spin function is required to ensure the correct doublet symmetry, and that the energy difference when using one or two spin functions should decrease to zero as the basis set is extended toward completeness. His reason for using the second spin function is that it is equivalent to introducing terms with a second set of exponential parameters, and the Fermi contact term had been shown to be very sensitive to such changes in the functional form of the wavefunction.

The benefit of the method is apparent when comparison is made with the value of the Fermi contact term for the largest basis set without and with the second spin function, 3.019 a_0^{-3} and 2.906 a_0^{-3} respectively. Although the latter value is in exact agreement with the experimental value to the number of figures quoted, the fluctuations in the calculated value as the basis set is enlarged have caused the convergence to be characterized as erratic³⁸.

The corresponding improvement in the ground state energy when the second spin function is included, -0.000015 a.u. , was relatively speaking much smaller, as expected, but the final eigenvalue itself, at -7.478025 a.u. , was nonetheless more than an order of magnitude improvement over the best previous value. Larsson, as well as other researchers^{20,56}, noted that the convergence of the ground state energy eigenvalue was rather slow toward the end of the expansion. This was a serious concern as the hand-selection of new terms to add to the expansion was basically a trial-and-error process based upon the energy improvement the new terms added, and this improvement was bound to differ depending upon the point in the expansion at which a particular new term was introduced.

Over the next decade the more efficient computational techniques were applied to the natural extensions of Larsson's work, with Hylleraas type variational calculations of excited ^2S states^{57,58}, the lowest and some excited $^2,^4\text{P}$ states and ^4S states⁵⁹⁻⁶² of lithium, and ground state calculations were undertaken for the lithium isoelectronic sequence⁶³. Hylleraas type wavefunctions were also applied to the ^1S ground state of beryllium⁶⁴.

Important steps were being taken in the development of many-body perturbation theory during the same period. Only a few months after Larsson's landmark 1968 work on the lithium ground state⁸, Chang et al.¹³ obtained a ground state energy of $-7.478 \pm 0.002 \text{ a.u.}$ and a value for the fermi contact term of $2.89 \pm 0.02 \text{ a}_0^{-3}$ using MBPT. By 1975, Garpman et al.⁶⁵ had improved the value

for the Fermi contact term to $2.9085 a_0^{-3}$, within 0.1 percent of the experimental result, treating the effect of the polarization of the closed shell to all orders of perturbation and correlation effects to lowest (third) order of the perturbation expansion.

The next calculations of the lithium ground state energy to approach, and finally surpass, Larsson's results adopted a conventional configuration interaction approach based upon the use of Slater type orbitals with the selected introduction of terms involving integral powers of the interelectronic coordinates r_{ij} . The "superposition of correlated configurations" [SCC] method was applied by Sims and Hagstrom⁶⁶ in 1975 to a calculation of the energies of the four lowest members of both the 2S and 2P series of lithium. The ground state energy obtained with a 150 term wavefunction was -7.478023 a.u., but of course the real importance of this work lay in the improved energy eigenvalues and wavefunctions obtained for the excited states when compared with previous calculations⁵⁷⁻⁵⁹. The configurations used to obtain this result provide an interesting comparison with the 59 term Hy wavefunction used by Larsson⁵⁸ in his study of the first four $(1s^2ns)$ 2S states of lithium. Starting with Slater type (ns) orbitals with n up to 5 suggested by Larsson's work, a 142 term wavefunction was constructed employing in each term at most one interelectronic coordinate r_{ij} with maximum power two. This improved upon the ground state energy of -7.477819 a.u. obtained by Larsson with the study wavefunction (which was carefully constructed to provide acceptable results while being a short enough expansion to be useful), lowering the eigenvalue obtained to -7.477973 atomic units. The eight terms which resulted in the final energy reduction of 0.000050 a.u. involved combinations p^2r_{ij} and $p^2r_{ij}^2$, comparable to including r_{ij}^3 and r_{ij}^4 in a straightforward Hylleraas type expansion. With only eight additional terms this reduction might seem incredibly large in light of the very slow convergence toward the end of Larsson's earlier 100 term expansion⁸, where

the last eight added terms yielded an energy reduction of only 0.000003 atomic units. The reason becomes clear when one realizes that Larsson's 59 term expansion, upon which Sims and Hagstrom patterned their 142 term wavefunction, had been built upon an extremely short (4 term) core representation. We are thus again reminded of James' and Coolidge's early conclusions about the continuing validity of a core-valence orbital picture when working with correlated basis sets.

In 1980 Muszynska et al.⁶⁷ applied the SCC method to a 139 term calculation of the lithium ground state. Their 2S wavefunction, which took 100 terms involving $(n_1s\ n_2s)\ n_3s'$ STO's with n_i only up to 4 and 39 $(n_1p\ n_2p)\ n_3s'$ STO's with $n_1, n_2 = 2, 3$ and combined them in products with a single correlation factor r_{ij} with powers up to 3, yielded a value of -7.478044 a.u. for the nonrelativistic ground state energy. Subsequently^{23,68} these SCC calculations were extended to the ground state and some excited states for members of the lithium isoelectronic sequence.

The following year Ho⁶⁹ applied Larsson's 60 term single spin-function expansion for the lithium ground state wavefunction to the calculation of ground state energies along the lithium isoelectronic sequence and also extended the wavefunction for the lithium ground state to include 92 terms, obtaining a value of -7.478031 for the energy eigenvalue.

In 1985, the MBPT calculation of Lindgren¹⁴ equaled the variational upper bound to the non-relativistic ground state energy of lithium obtained by Muszynska et al. in 1980. Lindgren also calculated a value for the hyperfine splitting that was only 0.3 percent larger than the experimental value. Subsequent relativistic MBPT calculations of the hyperfine splitting by Panigrahy et al.⁷⁰ and by Blundell et al.¹⁵ give values in fairly close agreement, but only about 0.2 percent larger than the observed splitting.

In 1986, King and Shoup⁹ made a very significant gain when they substantially increased the size of the Hylleraas type basis set used. With a 352

term wavefunction that employed both spin functions, they obtained an upper bound on the nonrelativistic ground state energy for lithium of -7.478058 a.u., and a value of 2.904079 a_0^{-3} for the Fermi contact term. In an attempt to study the convergence of the energy expectation value, these authors tried to adopt a more unbiased approach to enlarging the basis set than pre-screening candidate terms for their energy improvement. Instead they attempted to include all possible permutations of the powers of the coordinates r_i and r_{ij} that added to a fixed sum. This method of systematically extending a basis set towards completeness has proven useful in convergence studies for two-electron systems. Unfortunately, the number of possible permutations of these powers increases much more rapidly in the three-electron case, and King and Shoup were forced to break off this programmed enlargement of the basis set after a sum of only four was reached, yielding 210 terms. The remaining terms were selected by first incorporating all missing terms used by Larsson⁸ and Perkins⁶³, and then reverting to manual selection based on a combination of experience and guesswork. This, together with the arbitrary selection of intermediate stages in the basis set expansion for which their results are presented (which are not directly tied to the fixed sums of powers mentioned above), makes it difficult to interpret the convergence patterns for the matrix elements calculated. Nonetheless, the convergence continued to appear very slow for both the energy and the Fermi contact term.

Later the same year, King⁷¹ calculated the specific mass shifts for the 2S ground states of ^7Li and ^6Li using the 352 term wavefunction. In 1988 the ground state of Be II was examined in a 401 term Hylleraas type expansion⁷².

In 1989, King¹⁰ extended the original basis set to a total of 602 terms and performed calculations for the Li isoelectronic series up to Ne VIII. The energy improvement for the nonrelativistic ground state energy of lithium with the additional 250 terms was only 3 microhartrees, and no change at all was reported for

the last 102 terms.

A slightly higher energy eigenvalue for the ground state of lithium was reported late in 1989 by Kleindienst and Beutner¹¹, who obtained a value -7.47805824 a.u. using the method of superposition of correlated configurations. Although they have published a rather limited description of their 310 term wavefunction, it appears to be similar to that of the present work in that five sets of different orbital exponents were employed.

A very small improvement, to -7.47805953 a.u., was obtained in 1990 by King and Bergsbaken¹² using a much shorter, but much more complex, expansion in which the exponential parameters for each new term were optimized as the term was added. The calculation was also different from previous efforts by King et al. in that the 296 term wavefunction employed used only one spin function, to test the idea, also being examined in the present work, that the use of the second spin may successfully be replaced by a more flexible and carefully optimized set of basis functions. King and Bergsbaken believe that their result is accurate to within 1 microhartree, a result that is confirmed by the present work.

3. DESCRIPTION OF CALCULATION

This chapter will provide a description of the various elements of the calculation. This shall begin with the identification of the Hamiltonian used and the form of the trial wavefunction. The details of the construction of the basis set are provided next, followed by a brief discussion of the method of variational minimization of the ground state energy and the identification of the form of the Fermi contact operator that is evaluated in this study.

This is followed by sections describing the calculation of the integrals necessary for the evaluation of the matrix elements of interest, and key computational techniques required to address their storage and manipulation. The chapter concludes with a section on steps taken to assure that the integrals are calculated accurately and that the numerical precision of the final results is clearly defined.

3.1 Hamiltonian and Form of Trial Wavefunction

The Hamiltonian employed is the usual non-relativistic Hamiltonian for three electrons in the field of a fixed nucleus of charge Z , expressed in atomic units,

$$H = \sum_{i=1}^3 \left(-\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} \right) + \sum_{i=1}^3 \sum_{j>i}^3 \frac{1}{r_{ij}}. \quad (3.1.1)$$

Since the wave function is spherically symmetric, angular momentum terms can be dropped and the kinetic energy may be expressed in terms of the independent coordinates $r_1, r_2, r_3, u_1 = r_{23}, u_2 = r_{13}$ and $u_3 = r_{12}$ as^{8,73}

$$T = -\frac{1}{2} \left[\sum_{i=1}^3 \left[\frac{\partial^2}{\partial r_i^2} + \frac{2}{r_i} \frac{\partial}{\partial r_i} + 2 \frac{\partial^2}{\partial u_i^2} + \frac{4}{u_i} \frac{\partial}{\partial u_i} \right] \right. \\ \left. + \sum_P \left[-\frac{r_i^2 + u_k^2 - r_j^2}{r_i u_k} \frac{\partial^2}{\partial r_i \partial u_k} + \frac{1}{2} \frac{u_i^2 + u_k^2 - u_j^2}{u_i u_k} \frac{\partial^2}{\partial u_i \partial u_k} \right] \right] \quad (3.1.2)$$

where the second sum is over the six permutations of the symmetric group S_3 for the set $\{i,j,k\} = \{1,2,3\}$.

The trial variational wavefunction ψ is constructed from the linear combination

$$\psi = \mathcal{A} \sum_{\sigma=1}^N \sum_{\mu=1}^{N_\sigma} C_{\sigma\mu} \phi_{\sigma\mu} \chi_{\sigma\mu} \quad (3.1.3)$$

where the spatial part of the wavefunction, $\phi_{\sigma\mu}$, is of the form

$$\phi_{\sigma\mu}(r_1, r_2, r_3, r_{23}, r_{31}, r_{12}) = r_1^{m_{1\sigma\mu}} r_2^{m_{2\sigma\mu}} r_3^{m_{3\sigma\mu}} r_{23}^{n_{23\sigma\mu}} r_{31}^{n_{31\sigma\mu}} r_{12}^{n_{12\sigma\mu}} \\ \times \exp(-\alpha_\sigma r_1 - \beta_\sigma r_2 - \gamma_\sigma r_3), \quad (3.1.4)$$

and the spin function $\chi_{\sigma\mu}$ is one of the two linearly independent spin functions

$$\chi_1 = \alpha(1)\beta(2)\alpha(3) - \beta(1)\alpha(2)\alpha(3) \quad (3.1.5a)$$

$$\text{and } \chi_2 = 2\alpha(1)\alpha(2)\beta(3) - \beta(1)\alpha(2)\alpha(3) - \alpha(1)\beta(2)\alpha(3) \quad (3.1.5b)$$

which together span the doublet spin space with $M_s = +\frac{1}{2}$. In equation (3.1.3), \mathcal{A} represents the three particle antisymmetrizer, N indicates the number of sets of

Table 3.1

Sample Basis Set Expansion "Profiles" With a Single Set of Exponential Parameters

K	Maximum number of terms with χ_1 only				Sample wavefunction profiles				
	Open shell		Closed shell		Larsson ⁸		King et al. ^{9,10}		
	New	Total	New	Total	χ_1 only	χ_1, χ_2	χ_1 only	χ_1, χ_2	χ_1, χ_2
0	1	1	1	1	1	1	1	1	1
1	6	7	4	5	4	6	4	6	6
2	21	28	13	18	12	21	13	21	21
3	56	84	32	50	15	25	32	56	56
4	126	210	70	120	13	22	70	126	126
5	252	462	136	256	9	15	63	69	252
6	462	924	246	502	5	9	19	23	37
7	792	1716	416	918	1	1	17	18	38
8	1287	3003	671	1589			11	11	25
9	2002	5005	1036	2625			10	10	19
10	3003	8008	1547	4172			9	9	17
11	4368	12376	2240	6412			2	2	4
Total					60	100	251	352	602

exponential parameters α_σ , β_σ and γ_σ being used, and N_σ is the number of terms within a given set σ .

3.2 Basis Set Selection

As mentioned in the introduction, a systematic method for selecting the members of the orbital basis set is critical to the success of matrix element convergence studies. The selection technique adopted here is to define the sum $K_{\sigma\mu}$ of the linear powers in the orbital term by

$$K_{\sigma\mu} \equiv m_{1\sigma\mu} + m_{2\sigma\mu} + m_{3\sigma\mu} + n_{23\sigma\mu} + n_{31\sigma\mu} + n_{12\sigma\mu} \quad (3.2.1)$$

and then include in the basis set all terms such that $K_{\sigma\mu} \leq K$ for some non-negative integer value K .

Although such a basis set approaches completeness as K tends to infinity, it has the serious drawback that the number of permutations of the linear powers mushrooms rapidly as K increases, as may be seen in Table 3.1. This table shows the number of terms possible in both open and closed shell models using a single set of exponential parameters, and a single spin function, for values of K up to eleven. Profiles which indicate the number of terms used out of the total incremental set introduced at each successive value of K are also given for a few wave functions determined by Larsson⁸ or by King et al.^{9,10} using either one or both doublet spin functions.

It is clear that in the absence of guidelines as to which types of term can be expected to contribute most to reducing the energy, selecting the most important of the new incremental terms at even moderate values of K , say six or seven, is a difficult problem. Even then, the "optimum" terms selected to improve the

variational minimization of the energy cannot be expected to be the "optimum" ones for the calculation of some other matrix element. In addition, terms dropped at an early stage of basis set construction may become important at a later stage. Rather than relying upon the trial and error selection from the large incremental (with K) term sets that most previous studies^{8-10,23,58,63,67,69} have employed, this work presents results only for complete sets of all possible terms encompassed by a given cutoff value for K. While lower energies for a given total basis set size are no doubt possible by the judicious selection of higher order (K) terms, the systematic presentation of results for complete K shells produces convergence patterns with a well-defined meaning.

Table 3.1 also draws attention to the difference in the sizes of open ($\alpha_\sigma \neq \beta_\sigma$) and closed ($\alpha_\sigma = \beta_\sigma$) shell basis sets using only a single spin function. Examination of the sample profiles suggests that the same difference in the number of new terms generated at each order of K is found between closed shell basis sets with one and two spin functions. The origin of the size differential in both cases is clarified by the following examination of the symmetry of the wavefunction, closely based upon a discussion by Larsson⁸.

If an orbital function ϕ is a member of the basis set, leading to the antisymmetrized function

$$\psi_1 = \mathcal{A}\{\phi \chi_1\} = A\{\phi(\alpha\beta\alpha - \beta\alpha\alpha)\}, \quad (3.2.2a)$$

then the addition of the two new functions ψ' and ψ'' formed by taking the permutations (13) and (23) of the spatial orbital function ϕ , i.e.

$$\psi' = \mathcal{A}\{(13)\phi \chi_1\} = -A\{\phi(\alpha\beta\alpha - \alpha\alpha\beta)\}, \quad (3.2.2b)$$

$$\text{and } \psi'' = \mathcal{A}\{(23)\phi \chi_1\} = -A\{\phi(\alpha\alpha\beta - \beta\alpha\alpha)\}, \quad (3.2.2c)$$

forms a linearly dependent trio. A linearly independent pair of functions within the doublet spin space can be formed by taking ψ_1 and

$$\begin{aligned}\psi_{12} &= \psi' - \psi'' = \mathcal{A}\{[(13) - (23)]\phi \chi_1\} \\ &= \mathcal{A}\{\phi(2\alpha\alpha\beta - \beta\alpha\alpha - \alpha\beta\alpha)\} = \mathcal{A}\{\phi \chi_2\}.\end{aligned}\quad (3.2.2d)$$

Since χ_2 possesses (12) symmetry, ψ_{12} will vanish if the orbital function ϕ also exhibits the same symmetry. Orbital functions which possess $1 \leftrightarrow 2$ interchange symmetry can only be used with spin function χ_1 . Furthermore, as previously mentioned, in a closed shell calculation the set of orbital functions used with spin function χ_1 may be restricted further since the action of the antisymmetrizer in a term such as ψ_1 implies that the symmetrized version of the orbital function ϕ will automatically be generated.

In particular, a closed shell calculation using only χ_1 permits the omission of orbitals with $i_{\sigma\mu} > j_{\sigma\mu}$. Terms with $i_{\sigma\mu} = j_{\sigma\mu}$ can only be used with χ_1 due to their intrinsic symmetry, and terms with $i_{\sigma\mu} < j_{\sigma\mu}$ can be used in calculations with either one or both doublet spin functions. The latter offers an economical method of enlarging the basis set in a closed shell calculation, since the same radial integrals can be used twice, with the two different spin weightings provided by the integration over spins. The size of the resulting basis set is then the same as in the corresponding open shell calculation using only spin function χ_1 , where the $i_{\sigma\mu} > j_{\sigma\mu}$ terms may no longer be omitted since all the exponential parameters are different.

Returning for a moment to closed shell calculations, Larsson noted that instead of including the second spin function via terms of the form of ψ_{12} , one could use either ψ' or ψ'' directly since these are linear combinations of ψ_1 and ψ_{12} . This amounts to using an antisymmetrized function based upon spin function χ_1 only but with an orbital function having the role of either (core) index 1 or 2 interchanged

with (valence) index 3. It is in this sense that the use of both spin functions is equivalent to using one spin function with two exponential sets of basis functions – a notion that is central to this paper.

In the first part of the present study, we explore the impact of moving from a closed shell to an open shell representation with a single spin function. In the second part, we examine the effect of using more than one exponential set with one spin function. While significant improvement is expected in the ground state energy eigenvalues obtained using multiple basis sets, the critical test will be the value of the Fermi contact term, where an even more dramatic improvement is anticipated.

A major reason for this optimism is the dramatic success of the doubled basis set method employed by Drake⁵⁻⁷ in calculations on a variety of states in the helium isoelectronic sequence. In these calculations, the introduction of a doubled set of orbital functions with different exponential parameters has improved the accuracy of the energies calculated by several orders of magnitude with basis sets much smaller than would otherwise have been required. This improvement is especially important since large basis sets with a single set of exponents tend to become linearly dependent, resulting in severe numerical cancellation. The second set of exponential parameters provides a much more economical way (in terms of size) of increasing the flexibility of the basis set while at the same time avoiding problems of linear dependence.

In addition, a physical interpretation can be given to the doubled basis sets. One pair of exponential parameters is generally very close to the screened hydrogenic values, while the other pair of values is larger and tends to increase linearly with K as the basis set is enlarged. The former describes the asymptotic region of the wavefunction, and corresponds to our usual picture of an atom in an independent particle model. The latter improves the flexibility of the wavefunction in the region close to the nucleus where correlation effects are most important.

This picture would also suggest that other features strongly dependent upon a very good description of the wavefunction in the region of the nucleus, such as the hyperfine structure, would similarly benefit from a calculation that builds into the wavefunction the different but naturally important distance scales. From this perspective, Larsson's good results for the Fermi contact term using both spin functions seem much more understandable, and the question of the need to use both spin functions to obtain good accuracy in this calculation appears to be worth revisiting.

In exploring the merits of this picture in a three-electron system, a multiple, as opposed to doubled, basis set is employed. Given the size of even a single basis set of moderate order, and the expectation that high orders must be reached to achieve the accuracies desired, it appears necessary to find some uniform selection criterion which will allow the size of the basis set to be kept to a manageable level. In the two-electron case, for example, where the radial part of the wavefunction involves terms of the form

$$\phi(r_1, r_2, r_{12}) = r_1^i r_2^j r_{12}^k \exp(-\alpha r_1 - \beta r_2),$$

the overall symmetry requirements for the wavefunction allow the exclusion of terms with $i > j$. Such a term would be equivalent to the same term with $i < j$, but with the roles of the exponential parameters α and β interchanged. In the present case, however, the presence of multiple correlation factors $r_{ij}^{n_{ij}}$ makes the same reduction impossible in general (although a similar reduction, excluding terms with $i_{\sigma\mu} > j_{\sigma\mu}$, would be possible if all correlation factors were raised to a common power).

A similar restriction may be applied, nonetheless, on an *ad hoc* basis in a way that is consistent with the notion of physically distinct distance scales that appears naturally in the doubled basis set method. Rather than simply repeating for each

set of non-linear exponential parameters the full set of orbitals obtained by taking all possible permutations of the linear powers, a partition of the full set of linear powers is formed instead, with each partition having a unique set of exponential parameters. The partition chosen for use with six sets (numbered by σ) of exponential parameters is as follows:

	$\sigma = 5:$	$m_3 \leq m_1 \leq m_2$	and	$n_{31} \leq n_{23} \leq n_{12}$	(3.2.3)
Core	$\sigma = 6:$	$m_3 \leq m_2 \leq m_1$	and	$n_{23} \leq n_{31} \leq n_{12}$	
	$\sigma = 1:$	$m_1 \leq m_2 \leq m_3$	and	$n_{12} \leq n_{31} \leq n_{23}$	
Mid-range	$\sigma = 3:$	$m_2 \leq m_1 \leq m_3$	and	$n_{12} \leq n_{23} \leq n_{31}$	
	$\sigma = 2:$	$m_1 \leq m_3 \leq m_2$	and	$n_{31} \leq n_{12} \leq n_{23}$	
Asymptotic	$\sigma = 4:$	$m_2 \leq m_3 \leq m_1$	and	$n_{23} \leq n_{12} \leq n_{31}$	

The rationale in constructing the partitions is to choose the correlation powers l , m and n in a manner that couples high powers of the radial coordinates r_i and r_j with a high power of the interelectronic coordinate r_{ij} . In the $\sigma = 1$ partition, for example, orbitals 2 and 3 are emphasized at large distances from the nucleus much more than orbital 1, and it is therefore most important to emphasize the corresponding (2 \leftrightarrow 3) correlation most strongly. An advantage of this definition of the partitions, which places the emphasis on the dominant type of correlation, is that it leads to the introduction of different distance scales for the different partition sets in a natural way.

Sets five and six, for example, have the largest values for the power of the interelectronic coordinate r_{12} and should therefore be best able to represent correlation effects within the core. Likewise, the powers of the valence orbital radius r_3 are most restricted in this set, indicating that the structure of this orbital is relatively unimportant within this partition. Thus we expect this set to have

very large values for the non-linear parameters α and β , which should increase in value as the size of the basis set is expanded as in the two-electron case, and a "normal" Slater value (near 0.65) for the valence orbital non-linear parameter γ .

Sets one and three, on the other hand, should emphasize the structure of the valence orbital (the power of r_3 is largest) and core-valence correlation effects (powers of r_{23} and r_{31} are largest). These correlation effects will be most important at intermediate distances where the overlap between the core and valence orbitals is the greatest. This overlap may be increased by either elevating a core electron to an excited state or by regarding the valence orbital as one that is less fully screened. Thus α or β may be expected to be smaller, and γ larger, than the usual Slater values.

Finally, sets two and four, which offer the most balanced (in terms of a core-valence picture of the ground state) orbital representation, are most naturally associated with the usual form of the wavefunction valid at larger distances, where the notion of screened orbitals has the most validity.

Thus the three pairs may be expected to be distinguished from one another by their "correlation range", giving the same kind of natural separation observed in the two-electron case. For the three-electron case, we expect an "asymptotic" pair (sets 2 and 4), a sharp-cutoff "core" pair (sets 5 and 6) and a "middle distance" pair (sets 1 and 3).

3.3 The Variational Calculation

The variational optimization of the energy is performed as an iterative two-step procedure. In the first step the linear coefficients $C_{\sigma\mu}$ are optimized for a starting selection of the N sets of exponential parameters by diagonalizing the Hamiltonian, determining the optimum trial wavefunction and the corresponding

variational upper bound to the ground state energy. In the second step an improved selection of the exponential parameter sets is made by employing Newton's method to estimate the zeroes of the first derivatives of the variational energy eigenvalue with respect to each of the exponential parameters.

The implicit dependence upon the coefficients in these first derivatives vanishes because they are stationary with respect to first order variations of the energy. The remaining explicit dependence which, taking the exponential parameter α_1 as an example, is given by

$$\begin{aligned} \frac{\partial E}{\partial \alpha_1} &= \frac{\partial}{\partial \alpha_1} \left\{ \langle \psi | H | \psi \rangle / \langle \psi | \psi \rangle \right\} \\ &= 2 \langle \psi | H - E | \frac{\partial \psi}{\partial \alpha_1} \rangle / \langle \psi | \psi \rangle, \end{aligned} \quad (3.3.1)$$

and this represents a straightforward analytic calculation. After two iterations with slightly differing pre-selected exponential parameter sets, the second derivatives are estimated by differencing. The values of the exponential parameters that will locate the minimum in the multi-dimensional energy surface $E(\alpha_1, \beta_1, \gamma_1, \dots, \alpha_N, \beta_N, \gamma_N)$ can then be estimated by Newton's method. The iterative process continues thereafter until the desired convergence in the energy eigenvalue is obtained.

In an isolated application of this procedure with a basis set of fixed size, there is no guarantee that the global minimum sought will be obtained by this process rather than a local minimum, and there is a significant risk of arriving at the latter. The only way to provide any real assurance that the true minimum has been found is to repeat the optimization process with a different starting point and successfully arrive at the same minimum energy value. Due to the heavy burden this project as a whole placed upon the available computing resources, this confirmation process has not been undertaken except in the lowest order calculations. However, by remaining near the optimum exponential parameter values determined at the preceding order K at each step in enlarging the basis set, which tend to form

systematic trends, it is unlikely that any improvement that might be gained by seeking out a nearby but potentially lower minimum energy value would come close to the improvement gained by the increase in basis set size.

3.4 The Fermi Contact Operator

The terms representing the magnetic dipole hyperfine interaction will be regarded here as a first order perturbation to the non-relativistic Hamiltonian of equation (3.1). They are given by the following sum of effective operators as described by Blinder⁷⁴:

$$H^{(1)} = g_e g_I \mu_B \mu_N \vec{I} \cdot \sum_{k=1}^3 \left[r_k^{-3} \vec{l}_k + \{3r_k^{-5} (\vec{s}_k \cdot \vec{r}_k) \vec{r}_k - r_k^{-3} \vec{s}_k\} + \frac{8\pi}{3} \delta(\vec{r}_k) \vec{s}_k \right], \quad (3.4.1)$$

where μ_B and μ_N are the Bohr and nuclear magnetons respectively, g_e is the electron g factor, \vec{I} is the nuclear spin, g_I is the nuclear g factor relative to μ_N (i.e., if the magnetic moment of the nucleus is expressed as $\vec{\mu} = g_I \mu_N \vec{I}$, then $g_I = \mu_I / I$), and \vec{r}_k , \vec{l}_k and \vec{s}_k are the position, orbital angular momentum and spin vectors of the k -th electron.

The three terms in this expression may be identified as an orbital part, a spin-dipolar part and the Fermi contact part determined by the value of the wavefunction at the nucleus. Only the last term contributes to the hyperfine interaction in the 2S ground state of lithium. Write the contact interaction as

$$H_c^{(1)} = \vec{I} \cdot \vec{T}, \quad (3.4.2)$$

$$\text{where} \quad \vec{T} = -\frac{2}{3} g_e g_I \mu_B \mu_N \sum_{k=1}^3 4\pi \delta(\vec{r}_k) \vec{s}_k \quad (3.4.3)$$

is an irreducible tensor of rank one with respect to the total electronic angular momentum \vec{J} . Consider the matrix elements $\langle aJM_J | \vec{T} | a'J'M_J' \rangle$ and $\langle aJM_J | \vec{J} | a'J'M_J' \rangle$ between states of the total electronic angular momentum. Since they possess the same dependence on the magnetic quantum numbers, the Wigner-Eckart theorem implies that any two such matrix elements are proportional to one another, with the constant of proportionality given by the ratio of their reduced matrix elements. Thus we may re-write the hyperfine contact interaction $H_{\text{c}}^{(1)}$ in terms of the effective operator

$$H_{\text{c}}^{(1)} = \lambda \vec{I} \cdot \vec{J}, \quad (3.4.4)$$

where λ is the required ratio $\langle aJ || \vec{T} || a'J' \rangle / \langle aJ || \vec{J} || a'J' \rangle$. The ratio λ is usually expressed as a product $hA_{J,J'}$, so that the factor $A_{J,J'}$ is given in units of frequency.

Use of the effective operator allows a straightforward calculation of the separation between adjacent hyperfine levels in a manner analogous to the Landé interval rule. For example, the diagonal matrix element between states coupling the electronic and nuclear angular momentum to form the total angular momentum $\vec{F} = \vec{I} + \vec{J}$ is

$$\begin{aligned} \langle IJFM_F | H_{\text{c}}^{(1)} | IJFM_F \rangle &= \lambda \langle IJFM_F | \vec{I} \cdot \vec{J} | IJFM_F \rangle \quad (3.4.5) \\ &= \frac{1}{2} \lambda \langle IJFM_F | \vec{F}^2 - \vec{I}^2 - \vec{J}^2 | IJFM_F \rangle \\ &= \frac{1}{2} \lambda [F(F+1) - I(I+1) - J(J+1)], \end{aligned}$$

so the splitting is given by

$$\begin{aligned} E(F) - E(F-1) &= \lambda F = hA_{J,F} \quad (3.4.6) \\ &= [\langle aJ || \vec{T} || aJ \rangle / \langle aJ || \vec{J} || aJ \rangle] F \\ &= [\langle aJ || \vec{T} || aJ \rangle / \{ (2J+1)(J+1)J \}^{\frac{1}{2}}] F \end{aligned}$$

The reduced matrix element of \vec{T} may be simplified in the usual way⁷⁵ by considering the similar proportionality between matrix elements of \vec{T} and the total spin \vec{S} . Let the ratio λ' be defined by

$$\langle LSJ || \vec{T} || LSJ \rangle = \lambda' \langle LSJ || \vec{S} || LSJ \rangle. \quad (3.4.7)$$

The reduced matrix element of the spin operator can be evaluated explicitly:

$$\begin{aligned} \langle LSJ || \vec{S} || LSJ \rangle &= \sqrt{3} (2J+1) \begin{Bmatrix} L & S & J \\ L & S & J \\ 0 & 1 & 1 \end{Bmatrix} \langle L || 1 || L \rangle \langle S || \vec{S} || S \rangle \\ &= \sqrt{3} (2J+1) \left[\frac{(-1)^{3(S+J)+L+1}}{\sqrt{3} \sqrt{2L+1}} \begin{Bmatrix} L & J & S \\ 1 & S & J \end{Bmatrix} \right] (\sqrt{2L+1}) (\sqrt{2S+1} \sqrt{S(S+1)}) \\ &= \frac{1}{2} [J(J+1) + S(S+1) - L(L+1)] \left[\frac{2J+1}{J(J+1)} \right]^{\frac{1}{2}}. \end{aligned} \quad (3.4.8)$$

To evaluate the ratio λ' , note that the same ratio must exist between matrix elements, i.e.

$$\langle LSJM_J | T_0^{(1)} | LSJM_J \rangle = \lambda' \langle LSJM_J | S_0^{(1)} | LSJM_J \rangle.$$

But the coupled state

$$|LSJM_J\rangle = \sum_{M_L, M_S} \langle LM_L SM_S | JM_J \rangle |LM_L SM_S\rangle$$

reduces for the "stretched" case where $M_J = L + S$ to a single term

$$|LSJ(L+S)\rangle = \langle LLSS | J(L+S) \rangle |LLSS\rangle,$$

so the equation above relating matrix elements between these states gives

$$\langle LLSS | T_0^{(1)} | LLSS \rangle = \lambda' \langle LLSS | S_0^{(1)} | LLSS \rangle = \lambda' S.$$

Thus,

$$\begin{aligned}\lambda' &= \langle LLSS | T_0^{(1)} | LLSS \rangle / S \\ &= \frac{2}{3} g_e g_I \mu_B \mu_N \langle LLSS | \sum_{k=1}^3 4\pi \ell(\vec{r}_k) s_{z_k} | LLSS \rangle / S.\end{aligned}\quad (3.4.9)$$

Denoting the matrix element in this expression by $f/2$, the hyperfine constant A_J is

$$\begin{aligned}A_J &= \langle LSJ | \vec{T} | LSJ \rangle / [h\{(2J+1)(J+1)J\}^{\frac{1}{2}}] \\ &= \lambda' \langle LSJ | \vec{S} | LSJ \rangle / [h\{(2J+1)(J+1)J\}^{\frac{1}{2}}] \\ &= \frac{2}{3} g_e g_I \mu_B \mu_N - \frac{f}{2} \frac{\frac{1}{2}[J(J+1) + S(S+1) - L(L+1)]}{SJ(J+1)}\end{aligned}\quad (3.4.10)$$

If we include the units (a_0^{-3}) of f in the leading constant and express the result in SI units, the following expression gives A_J in MHz:

$$A_J = G \frac{g_e \mu_1}{3I} \frac{f}{2} \frac{\frac{1}{2}[J(J+1) + S(S+1) - L(L+1)]}{SJ(J+1)}, \quad (3.4.11)$$

where $G = \left[\frac{\mu_0 \mu_B \mu_N}{2\pi h a_0^3} \right]$. Adopting the values of μ_B , μ_N , h and a_0 given by Cohen

and Taylor⁷⁶ in the most recent adjustment of fundamental physical constants,

$G = 95.41067(7)$ MHz. For the ground state of lithium, $F = 2$, $I = 3/2$, $L = 0$ and $J = S = 1/2$, so the hyperfine splitting in MHz is related to A_J by the expression

$$\nu/2 = A_J = G \frac{g_e \mu_1}{3I} f. \quad (3.4.12)$$

Using the experimental values⁷⁷ $\nu = 803.504\,086\,6(10)$ MHz, $\mu_1 = 3.256416$

nuclear magnetons and $g_e = 2.0023019$, an experimental value for f of 2.906058 a.u.

is obtained.

There is some inconsistency in the literature as to whether the appropriate value for the electron g factor for use in this calculation is the Dirac value ($g = 2$) or a value including Q.E.D. corrections. Chang et al.¹³, for example, gave a value for the experimental value of f that is clearly based upon the value $g = 2$, even though they quote the value of the Q.E.D. corrected g factor. Lindgren¹⁴ also uses $g = 2$ to calculate an experimental value of f for comparison with the theoretical calculations of a number of authors. This value for g seems inappropriate.

It was in fact the observed discrepancies in the hyperfine splitting of the $1S_{\frac{1}{2}}$ ground state of hydrogen that stimulated Breit⁷⁸ in 1947 to suggest that a quantum electrodynamic correction to the Dirac g factor of order α was necessary. The following year, in the third paper of Schwinger's series on a covariant formulation of quantum electrodynamics⁷⁹, Breit's suggestion was confirmed when Schwinger derived the first order correction to the spin magnetic moment of the electron by considering the current induced in the vacuum by a spinning electron, and found a fractional increase by a factor of $\alpha/2\pi$. Several higher orders of corrections have been calculated since.

It is clear that these Q.E.D. corrections must be taken into account to relate the present non-relativistic calculation meaningfully to the experimentally observed hyperfine splitting of the lithium ground state. The only question that can arise is whether to use the free-electron g factor or some other value which better takes into account the actual corrections for this state. The choice made here is to use the experimental value obtained from the observed Zeeman structure, which is within 0.001 percent of the free-electron g factor value,

$$g = 2(1 + \alpha/2\pi + O(Z\alpha^2)) = 2.002319...$$

Support for this selection may be found in the analysis of the hyperfine structure of the 2^3P state of ^3He given by Hinds et al.⁸⁰. These authors define a

non-relativistic Fermi contact coupling constant C in terms of matrix elements of the delta function which are known theoretically to high precision, obtaining the value $C = -4281.723$ MHz. This value does not take into account corrections for relativistic and radiative effects or for the effects of nuclear size or finite nuclear mass. Allowing for the last effect using the reduced mass correction factor 0.9994556 gives a mass-corrected value of $C' = -4279.392$ MHz for this coupling constant.

The experimental value for this constant, determined by Prestage et al.⁸¹, is $C_{\text{exp}} = -4279.292$ MHz, leading to an effective value for the electron g factor given by the ratio

$$g_{\text{eff}} = 2 \frac{C_{\text{exp}}}{C'} = 2.00208(1).$$

This may be compared with the value 2.00224 obtained from the observed Zeeman structure⁸².

Again, these values are very close to the free-electron g factor, and suggest that the "correct" g factor value to use in the present study may be stated as

$$g = 2.0023(2).$$

If this value of g is used to calculate the experimental value for the Fermi contact term for the ground state of lithium, the value obtained is

$$f = 2.9061(3).$$

In view of the very slight difference between the g factor obtained from the Zeeman splitting in lithium and the free electron value, we may be confident that the above error limits on the experimental f value are generous.

3.5 Calculation of Integrals

Define the function

$$\begin{aligned} \phi(j_1, j_2, j_3, \nu_{23}, \nu_{31}, \nu_{12}) &= r_1^{j_1} r_2^{j_2} r_3^{j_3} r_{23}^{\nu_{23}} r_{31}^{\nu_{31}} r_{12}^{\nu_{12}} \\ &\times \exp(-\alpha r_1 - \beta r_2 - \gamma r_3). \end{aligned} \quad (3.5.1)$$

Then all required integrals except those required for matrix elements involving the delta function are of the form

$$\begin{aligned} I &= \int d^3v \phi(j_1, j_2, j_3, \nu_{23}, \nu_{31}, \nu_{12}) \\ &\times Y_{l_1}^{m_1'}(\hat{r}_1)^* Y_{l_2}^{m_2'}(\hat{r}_2)^* Y_{l_3}^{m_3'}(\hat{r}_3)^* Y_{l_1}^{m_1}(\hat{r}_1) Y_{l_2}^{m_2}(\hat{r}_2) Y_{l_3}^{m_3}(\hat{r}_3). \end{aligned} \quad (3.5.2)$$

Perkins⁵⁵ gives the following expansion for r_{12}^ν :

$$r_{12}^\nu = \sum_{q=0}^{L_1} P_q(\cos \theta_{12}) \sum_{k=0}^{L_2} C_{\nu q k} s_{12}^{q+2k} g^{\nu-q-2k}, \quad (3.5.3)$$

where s_{12} and g_{12} are the smaller and greater, respectively, of r_1 and r_2 , the summation upper limits L_1 and L_2 are

$$L_1 = \begin{cases} n/2 \\ \infty \end{cases} \quad \text{and} \quad L_2 = \begin{cases} n/2 - q \\ (n+1)/2 \end{cases} \quad \text{as } \nu \text{ is } \begin{cases} \text{even} \\ \text{odd} \end{cases}, \quad (3.5.3a)$$

and the coefficients $C_{\nu q k}$ are given by

$$C_{\nu q k} = \frac{(2q+1)}{(\nu+2)} \left[\begin{matrix} n+2 \\ 2k+1 \end{matrix} \right] \prod_{t=0}^{S_{qv}} \frac{(2k-2t-n)}{(2k+2q-2t+1)}, \quad (3.5.3b)$$

where S_{qv} is the smaller of $(q-1)$ and the integral part of $[(\nu+1)/2]$. Denoting the innermost summand in (3.5.3) for brevity as $F(\nu, q, k)_{12}$, we find that upon expanding each of the correlation factors in (3.5.2) in this way, the integral may be expressed as

$$\begin{aligned} I = & \sum_{q_{23}=0}^{L_{23}^1} \sum_{k_{23}=0}^{L_{23}^2} \sum_{q_{31}=0}^{L_{31}^1} \sum_{k_{31}=0}^{L_{31}^2} \sum_{q_{12}=0}^{L_{12}^1} \sum_{k_{12}=0}^{L_{12}^2} \times \\ & \int d^3r \phi(j_1, j_2, j_3, \nu_{23}, \nu_{31}, \nu_{12}) F(\nu, q, k)_{12} F(\nu, q, k)_{23} F(\nu, q, k)_{31} \\ & \times \int d^3\Omega Y_{l_1}^{m_1'}(\hat{r}_1)^* Y_{l_2}^{m_2'}(\hat{r}_2)^* Y_{l_3}^{m_3'}(\hat{r}_3)^* P_{q_{23}}(\cos \theta_{23}) P_{q_{31}}(\cos \theta_{31}) P_{q_{12}}(\cos \theta_{12}) \\ & \times Y_{l_1}^{m_1}(\hat{r}_1) Y_{l_2}^{m_2}(\hat{r}_2) Y_{l_3}^{m_3}(\hat{r}_3). \end{aligned} \quad (3.5.4)$$

The angular part of this integral, which shall be referred to as integral A in the following, may be simplified using the relations

$$P_k(\cos \theta_{ab}) = \sum_q C_q^{(k)*}(\hat{r}_1) C_q^{(k)}(\hat{r}_2) = \sum_q (-1)^q C_q^{(k)}(\hat{r}_1) C_q^{(k)}(\hat{r}_2) \quad (3.6a)$$

and

$$\begin{aligned} C_q^{(k)}(\hat{r}) C_{q'}^{(k')}(\hat{r}) = & \sum_{k''} C_{q''}^{(k'')*}(\hat{r}) (2k'' + 1) (-1)^{q''} \begin{bmatrix} k & k' & k'' \\ q & q' & -q'' \end{bmatrix} \begin{bmatrix} k & k' & k'' \\ 0 & 0 & 0 \end{bmatrix} \\ & (\text{with } q'' = q + q'), \end{aligned} \quad (3.6b)$$

where $C_q^{(k)}(\hat{r})$ represents the q component of the k -th order Racah tensor, related to

the spherical harmonics by

$$C_q^{(k)}(\hat{r}) = \left[\frac{4\pi}{2k+1} \right]^{1/2} Y_k^q(\hat{r}).$$

Expanding the Legendre functions in (3.5.4) using (3.6a) and combining each corresponding pair of resulting Racah tensors, the angular integral A becomes

$$\begin{aligned} A = & \sum_{n_{ij}} (-1)^{n_{12}+n_{23}+n_{31}} \sum_{k_i} (2k_i+1) \begin{bmatrix} q_{12} & q_{31} & k_1 \\ -n_{12} & n_{31} & -q_1 \end{bmatrix} \begin{bmatrix} q_{12} & q_{31} & k_1 \\ 0 & 0 & 0 \end{bmatrix} \\ & \times (2k_2+1) \begin{bmatrix} q_{23} & q_{12} & k_2 \\ -n_{23} & n_{12} & -q_2 \end{bmatrix} \begin{bmatrix} q_{23} & q_{12} & k_2 \\ 0 & 0 & 0 \end{bmatrix} (2k_3+1) \begin{bmatrix} q_{31} & q_{23} & k_3 \\ -n_{31} & n_{23} & -q_3 \end{bmatrix} \begin{bmatrix} q_{31} & q_{23} & k_3 \\ 0 & 0 & 0 \end{bmatrix} \\ & \times \int d^3\Omega Y_{l_1}^{m_1'}(\hat{r}_1)^* Y_{l_2}^{m_2'}(\hat{r}_2)^* Y_{l_3}^{m_3'}(\hat{r}_3)^* C_{q_1}^{(k_1)}(\hat{r}_1) C_{q_2}^{(k_2)}(\hat{r}_2) C_{q_3}^{(k_3)}(\hat{r}_3) \\ & Y_{l_1}^{m_1}(\hat{r}_1) Y_{l_2}^{m_2}(\hat{r}_2) Y_{l_3}^{m_3}(\hat{r}_3) \quad (3.7) \end{aligned}$$

The remaining angular integral in (3.7), which will be referred to as A_1 , is a simple product of three elementary angular integrals, which may be expressed using the c^k coefficient of Condon and Shortley as

$$\langle lm | C_q^{(k)} | l' m' \rangle = c^k(lm, l' m') \delta_{q, m-m'}$$

where

$$c^k(lm, l' m') = (-1)^m \sqrt{(2l+1)(2l'+1)} \begin{bmatrix} l & l' & k \\ -m & m' & q \end{bmatrix} \begin{bmatrix} l & l' & k \\ 0 & 0 & 0 \end{bmatrix},$$

in which the sum $l+l'+k$ must be even for the integral to be non-zero. In terms of these coefficients, the angular integral a may be expressed as

$$\begin{aligned}
A = & \sum_{n_{ij}} (-1)^{n_{12}+n_{23}+n_{31}} \\
& \times \sum_{k_i} (-1)^{n_{12}} \frac{(2k_1+1)}{\sqrt{(2q_{12}+1)(2q_{31}+1)}} c^{k_1(q_{12}n_{12}, q_{31}n_{31})} \delta_{q_1, n_{31}-n_{12}} \\
& \times (-1)^{n_{23}} \frac{(2k_2+1)}{\sqrt{(2q_{23}+1)(2q_{12}+1)}} c^{k_2(q_{23}n_{23}, q_{12}n_{12})} \delta_{q_2, n_{12}-n_{23}} \\
& \times (-1)^{n_{31}} \frac{(2k_3+1)}{\sqrt{(2q_{31}+1)(2q_{23}+1)}} c^{k_3(q_{31}n_{31}, q_{23}n_{23})} \delta_{q_3, n_{23}-n_{31}} \\
& \times c^{k_1(l_1 m_1, l_1' m_1')} \delta_{q_1, m_1-m_1'} c^{k_2(l_2 m_2, l_2' m_2')} \delta_{q_2, m_2-m_2'} \\
& \times c^{k_3(l_3 m_3, l_3' m_3')} \delta_{q_3, m_3-m_3'}
\end{aligned}$$

Regarding q_1, q_2, q_3 as predetermined fixed values, only a single summation over one n_{ij} value is needed. Choosing n_{12} arbitrarily,

$$\begin{aligned}
A = & [(2q_{12}+1)(2q_{23}+1)(2q_{31}+1)]^{-1} \times \sum_{n_{12}=-q_{12}}^{q_{12}} \sum_{k_p} (2k_1+1)(2k_2+1)(2k_3+1) \\
& \times c^{k_1(q_{12}, n_{12}; q_{31}, n_{12}+q_1)} c^{k_2(q_{23}, n_{12}-q_2; q_{12}, n_{12})} c^{k_3(q_{31}, n_{12}+q_1; q_{23}, n_{12}-q_2)} \\
& \times c^{k_1(l_1 m_1, l_1' m_1')} \delta_{q_1, m_1-m_1'} c^{k_2(l_2 m_2, l_2' m_2')} \delta_{q_2, m_2-m_2'} \\
& \times c^{k_3(l_3 m_3, l_3' m_3')} \delta_{q_3, m_3-m_3'}
\end{aligned}$$

In this expression, the Kronecker deltas imply that a non-zero value of A occurs only for a selection of the q_i 's that sum to zero. Similarly, the 3-j symbols in the Condon coefficients require that all of the sums

$$\begin{array}{ll} l_1 + l_1 + k_1, & q_{12} + q_{31} + k_1, \\ l_2 + l_2 + k_2, & q_{23} + q_{12} + k_2 \quad \text{and} \\ l_3 + l_3 + k_3, & q_{31} + q_{23} + k_3 \end{array}$$

must be even if the integral is not to vanish.

Thus the integral I may be written

$$\begin{aligned} I &= \sum_{\substack{q_{12} \\ k_{12}}} \sum_{\substack{q_{23} \\ k_{23}}} \sum_{\substack{q_{31} \\ k_{31}}} A(q_{12}, q_{23}, q_{31}) \times \int d^3r \phi F_{12} F_{23} F_{31} \\ &= \sum_{\substack{q_i \\ k_i}} A(q_{12}, q_{23}, q_{31}) C_{\nu_{12}, q_{12}, k_{12}} C_{\nu_{23}, q_{23}, k_{23}} C_{\nu_{31}, q_{31}, k_{31}} \\ &\quad \times \int d^3r \phi (s_{12}^{p_{12}} g_{12}^{t_{12}}) (s_{23}^{p_{23}} g_{23}^{t_{23}}) (s_{31}^{p_{31}} g_{31}^{t_{31}}), \end{aligned}$$

where

$$p_{ab} = q_{ab} + 2k_{ab}; \quad t_{ab} = \nu_{ab} - p_{ab}.$$

The radial integral may be evaluated by breaking up the region of integration into six parts depending upon the relative magnitudes of r_1 , r_2 and r_3 . The resulting integrals are all of the form

$$W(l, m, n; a, \beta, \gamma) = \int_0^\infty dx x^l e^{-ax} \int_x^\infty dy y^m e^{-\beta y} \int_y^\infty dz z^n e^{-\gamma z}.$$

Their evaluation is discussed in Appendix 1.

In the case of S states, the angular integral is particularly simple, with a value

$$A = (2q_{12}+1)^{-2} \delta_{q_{12},q_{23}} \delta_{q_{23},q_{31}}.$$

The expression for the complete integral I reduces in this case from a sixfold summation to the double sum

$$I = \sum_{q_{12}=0}^{L_{12}^1} (2q_{12}+1)^{-2} \sum_{k_{12}=0}^{L_{12}^2} \int d^3r \phi F(\nu_{12},q_{12},k_{12}) F(\nu_{23},q_{12},k_{23}) F(\nu_{31},q_{12},k_{31}).$$

An important special case occurs when any ν_{ij} is zero, for then the corresponding L_{ij}^i limit is zero also, and the Kronecker deltas which link the q_{ij} values imply that all the q_{ij} 's are similarly restricted. Thus, for example,

$$\begin{aligned} I(\nu_{12},0,0) &= \sum_{q_{12}=0}^{L_{12}^1} (2q_{12}+1)^{-2} \sum_{k_{12}=0}^{L_{12}^2} \int d^3r \phi F(\nu_{12},q_{12},k_{12}) F(0,0,0) F(0,0,0) \\ &= \int d^3r \phi F(\nu_{12},0,0) = \int d^3r \phi C_{\nu_{12},0,0} s_{12}^0 g_{12}^{\nu_{12}} = \int d^3r \phi g_{12}^{\nu_{12}}. \end{aligned}$$

Not only has the undesirable case where I involves an infinite series been avoided, but the actual integral involved can be represented by a closed-form analytic expression for all values of the parameters in ϕ which are actually encountered.

Although a similar series truncation occurs whenever even a single ν_{ij} is even, the basis set used to generate only such truncated integrals would have to be restricted

to terms with at least two even correlation powers. This has been an important consideration in previous studies. In the set of sixty orbital basis functions selected by Larsson⁸, for example, only two terms did not meet this condition. All others, in fact, had at least two of the correlation powers equal to zero. Subsequent works have similarly tended to favour such terms in the basis set, keeping the number of terms with "linked" correlation indices small. Although Larsson recognized that the inclusion of such "linked" terms is necessary to ensure completeness of the basis, he found that they were of little importance for the energy⁵⁸. Their inclusion is important, however, if the wavefunction is to have the correct analytic form and in particular, if it is to satisfy the cusp conditions^{83,84} that are associated with the vanishing of the various interparticle distance coordinates. Furthermore, the recent results of Kleindienst and Beutner¹¹ suggest that terms with linked correlation indices are responsible for a contribution of approximately 14 μ hartrees to the non-relativistic lithium ground state energy, almost independent of the basis set dimension.

The integral corresponding to I given by (3.5.2) with a delta function inserted has the advantage that it may always be evaluated analytically in closed form. As an example, consider the integral given by

$$\begin{aligned}
 I_{\delta_3} &= \int d^3v \phi(j_1, j_2, j_3, \nu_{23}, \nu_{31}, \nu_{12}) \delta(\vec{r}_3) \\
 &\times Y_{l_1}^{m_1'}(\hat{r}_1)^* Y_{l_2}^{m_2'}(\hat{r}_2)^* Y_{l_3}^{m_3'}(\hat{r}_3)^* Y_{l_1}^{m_1}(\hat{r}_1) Y_{l_2}^{m_2}(\hat{r}_2) Y_{l_3}^{m_3}(\hat{r}_3) \\
 &= \int d\vec{r}_1 \int d\vec{r}_2 \left[r_1^{j_1} r_2^{j_2} r_{12}^{\nu_{12}} \exp(-\alpha r_1 - \beta r_2) \right] \\
 &\times Y_{l_1}^{m_1'}(\hat{r}_1)^* Y_{l_2}^{m_2'}(\hat{r}_2)^* Y_{l_1}^{m_1}(\hat{r}_1) Y_{l_2}^{m_2}(\hat{r}_2) \\
 &\times \int r_3^2 d\vec{r}_3 \left[r_3^{j_3} r_{23}^{\nu_{23}} r_{31}^{\nu_{31}} \exp(-\gamma r_3) \right] \frac{\delta(r_3)}{4\pi r_3^2} \\
 &\times \int \sin \theta_3 d\theta_3 d\phi_3 Y_{l_3}^{m_3'}(\hat{r}_3)^* Y_{l_3}^{m_3}(\hat{r}_3)
 \end{aligned}$$

$$I_{\delta_3} = \delta_{j_3,0} \int d\vec{r}_1 \int d\vec{r}_2 \left[r_1^{j_1+\nu_{31}} r_2^{j_2+\nu_{23}} r_{12}^{\nu_{12}} \exp(-\alpha r_1 - \beta r_2) \right] \\ \times Y_{l_1}^{m_1'}(\hat{r}_1)^* Y_{l_2}^{m_2'}(\hat{r}_2)^* Y_{l_1}^{m_1}(\hat{r}_1) Y_{l_2}^{m_2}(\hat{r}_2)$$

The remaining double integral is a particular example of a two-electron integral which is described, for example, by Drake⁸⁵. Adopting his notation, this integral is given by

$$I_{\delta_3} = \frac{\delta_{j_3,0}}{8\pi} I_0(j_1+\nu_{31}, j_2+\nu_{23}, \nu_{12}, a, \beta)$$

where

$$I_0(a-1, b-1, c-1, a, \beta) = \int_0^\infty dr_1 \int_0^\infty dr_2 \int_{|r_1-r_2|}^{r_1+r_2} dr_{12} r_1^a r_2^b r_{12}^c \exp(-\alpha r_1 - \beta r_2)$$

This integral is readily evaluated by breaking up the region of integration into two parts depending upon which of r_1 or r_2 is greater and applying the binomial expansion to the integration over r_{12} . The result is

$$I_0(a-1, b-1, c-1, a, \beta) = \frac{2}{c+1} \sum_{i=0}^{(c/2)} \left[\begin{matrix} c+1 \\ 2i+1 \end{matrix} \right] \left\{ \sum_{j=0}^q \frac{q! (p+j)!}{\beta^{q-j+1} (a+\beta)^{p+j+1} j!} \right. \\ \left. + \sum_{j=0}^{q'} \frac{q'! (p'+j)!}{a^{q'-j+1} (a+\beta)^{p'+j+1} j!} \right\},$$

where $(c/2)$ is the largest integer in $c/2$, and

$$p = a + 2i + 1,$$

$$q = b + c - 2i,$$

$$p' = b + 2i + 1$$

$$\text{and } q' = a + c - 2i.$$

3.6 Computational Techniques

The efficient use of computing resources is critical to the success of the study of three-electron systems using the algorithms described previously.

As the potential for (in principle) infinite series arises in both the calculation of the complete radial integrals I (in the case where all powers of the interelectronic distances r_{ij} are odd) and the subsidiary integrals W (when the power of r for the innermost integrand is negative), it is important to avoid recalculating these integrals wherever possible. As an example of the computational savings possible, for the case of the W integrals mentioned above, only a few percent of the function (integral) calls actually represent new integrals that must be evaluated from scratch if some means of tabulating and accessing the computed values is available. Thus the major elements of computational strategy to be considered in undertaking these calculations are first, the efficient calculation of the time-consuming integrals, and second, their efficient storage and retrieval for subsequent re-use.

The technique employed here for the integrals mentioned above is to calculate the value of any required integral once and store the value in a linear array for access as required later using an algorithm for a balanced tree search and insertion described by Knuth⁸⁶. The method is, in essence, a binary search of a tree structure for the node representing the desired integral. The tree structure is, however, balanced in the sense that the branches are never allowed to differ too much in length as they grow with the addition of new nodes, keeping the search times much lower, on average, than for an unbalanced tree structure.

To be most effective, this array should be maintained in the best location for high-speed access, which in the present instance means the main RAM memory of the computer rather than random access disk storage. To maximize the availability of the main computer memory for these integrals, the completed Hamiltonian and

overlap integrals were stored on disk in conveniently sized blocks. The algorithm used to solve the resulting symmetric system of linear equations, the square root method⁸⁷, was adapted to allow the solution to proceed one row at a time⁸⁸, minimizing main memory requirements. Rather than performing a complete matrix diagonalization using a Jacobi or Householder process, the power method⁸⁹ was used to iteratively converge upon the lowest eigenvalue and corresponding eigenvector.

The program that has been developed has proven to be (or more correctly has evolved to be) very flexible in terms of the computing resources available, in that, as long as adequate disk storage is available, fairly modest main computer memory is required to perform a calculation. Much of the development work was done on an IBM AT class personal computer, and low-order single and multiple exponential set open-shell calculations were first performed on a Definicon DSI-020 co-processor board (which is based upon a Motorola 68020 processor with 4 Mb of memory) installed in such a PC. Computational speed, rather than space, concerns ultimately dictated the move to a higher speed machine. While supercomputing resources were considered, an engineering workstation was selected as being a more cost effective solution. A Sun Sparcstation 1 workstation has been used to complete the calculations in this study.

3.7 Accuracy Concerns

The importance of stringent accuracy control in this type of calculation was addressed by Bunge²⁰ in an analysis of Larsson's results⁸. In his study, Larsson calculated all radial (I) integrals to ten significant figures. Bunge pointed out that while this was likely sufficient to ensure an accuracy of seven to nine figures for the energy eigenvalue, the eigenvector was probably accurate to no more than five

figures, so that random fluctuations of about $0.002 a_0^{-3}$ could be possible in Larsson's value for the Fermi contact term. This was precisely the level of fluctuation remaining in the values of this parameter at the end of Larsson's series of calculations.

In the present set of calculations the convergence criterion for individual integrals was set at 1 part in 10^{16} . This should permit the calculation of the energy eigenvalue to twelve or thirteen figures and the Fermi contact term to approximately seven significant figures. To check the numerical stability of the computational results, the calculations were repeated with a slightly lower convergence criterion specified, 1 part in 10^{14} . This value was selected for comparison with the experience of King and Shoup⁹, who found that all calculated expectation values were unchanged to seven significant figures when matrix element input was reduced from 18 to 14 significant figures, with changes occurring typically in the ninth to eleventh figure. In general, the experience in this study for basis sets of comparable size (under 400 terms) was similar, but for some of the larger size basis sets of the current study, the Fermi contact term and the matrix element $\langle r_i^{-3} \rangle$ displayed changes in the sixth digit due to changes actually attributable to changes in the seventh significant figure. Furthermore, in open-shell calculations using a single exponential set with only one spin function, the impact of near linear-dependence of terms in the basis set became quite apparent, producing a marked reduction in the number of significant figures accessible when the core exponential parameters were not sufficiently distinct. Note that the partitioning method adopted in constructing multiple basis sets avoids this problem for the majority of cases.

To ensure that the algorithms themselves were reliable, a number of benchmark calculations were performed. In a number of cases of the A , V and W integrals, analytic results could be calculated to use for comparisons. For the

"infinite series" forms of the W and I integrals comparisons were made to published results of both Öhrn and Nordling⁵³ and Ho and Page⁹⁰. Finally a number of selected single exponential set, single spin function were undertaken to confirm that the combined package of integration and linear equation routines performed properly, including several of the calculations from Larsson's 1968 study⁸, the 92-term calculation of Ho⁶⁹ and the 50-term ($K = 3$) calculation of King and Shoup⁹.

4. RESULTS AND DISCUSSION

The results of calculations employing single and multiple sets of exponential parameters respectively are presented in the following two sections. Note that all calculations done in the present study employ a single spin function (χ_1).

The notation adopted for expectation values conforms with that used by King et al.^{9,10,12}, i.e.,

$$\langle a_i \rangle = \left\langle \psi \left| \sum_{i=1}^3 a_i \right| \psi \right\rangle,$$

and

$$\langle a_{ij} \rangle = \left\langle \psi \left| \sum_{i=1}^3 \sum_{j \neq i}^3 a_{ij} \right| \psi \right\rangle$$

where the wavefunction ψ is assumed to be normalized.

While the main emphasis is on the energy eigenvalues and the Fermi contact term

$$f = \langle 4\pi \delta(\vec{r}_i) \sigma_{zi} \rangle,$$

a few moments of r_i and r_{ij} are also presented, as well as the electron density at the nucleus, given by

$$\rho(0) = \langle \delta(\vec{r}_i) \rangle.$$

All matrix elements have been appropriately scaled using the scale factor η deduced from the virial theorem, i.e.,

$$\eta = - \frac{\frac{1}{2} \langle V \rangle}{\langle T \rangle}.$$

This is equivalent to replacing all distances r by the scaled value $r' = r/\eta$, which will force the ratio of expectation values above to equal one and satisfy the virial theorem.

Each matrix element shown has been rounded to include the least significant

Table 4.1.1

(1s)²2s ²S Li Energy Eigenvalues Using a Single Set of Exponential Parameters

Fixed closed-shell exponents ^a					Optimized open-shell exponents
K	One spin function ^b		Two spin functions ^c		One spin function ^b
	No. of Terms	Energy (a.u.)	No. of Terms	Energy (a.u.)	Energy (a.u.)
1	5	-7.452 755 892 519 1	7		-7.466 005 824 265
2	18	-7.474 645 160 892 41	23	-7.475 984	-7.477 286
3	50	-7.477 788 518 162 7	84	-7.477 845	-7.477 933 616
4	120	-7.477 988 936 406	210	-7.478 006	-7.478 034 552
5	256	-7.478 037 271 2	462		-7.478 053 7

a. To facilitate comparison with other calculations, the fixed closed-shell exponents are chosen to be those of Larsson (ref. 8), i.e. $\alpha = \beta = 2.76$, $\gamma = 0.65$. The "optimized" open-shell exponents are detailed in Figure 4.1.1 and Table 4.1.4.

b. Present work

c. F. W. King and V. Shoup., Phys. Rev. A, 33, (1986) 2940

Table 4.1.2

(1s)²2s ²S Li Scale Factor Using a Single Set of Exponential Parameters

K	Fixed closed-shell exponents ^a				Optimized open-shell exponents
	One spin function ^b		Two spin functions ^c		One spin function ^b
	No. of Terms	$\eta - 1$	No. of Terms	$\eta - 1$	$\eta - 1$
1	5	3.27 [-3]	7		6.35 [-7]
2	18	9.10 [-5]	28	7.3 [-5]	- 3.11 [-7]
3	50	1.57 [-4]	84	1.11 [-4]	- 3.26 [-7]
4	120	2.71 [-5]	210	2.3 [-5]	- 1.02 [-7]
5	256	9.63 [-6]	462		- 4.11 [-7]

a. $\alpha = \beta = 2.76$, $\gamma = 0.65$. b. Present work.c. F. W. King and V. Shoup., Phys. Rev. A, 33, (1986) 2940

digit which first shows a change when the convergence criterion for the calculation of the radial integrals was reduced from 1 part in 10^{16} to 1 part in 10^{14} .

4.1 Calculations Using a Single Exponential Set

The energy eigenvalues obtained are presented first in Table 4.1.1. Three sets of values are shown to illustrate clearly the impact of moving from a closed-shell representation with fixed parameters to an open-shell representation in which the non-linear exponential parameters have been optimized to provide the lowest variational ground state energy. For purpose of comparison, the three comparable values obtained by King and Shoup⁹ using a closed-shell representation with the same fixed exponential parameters, but using both spin functions, are presented. (Recall from the discussion of the basis set in section 3.2 that the number of terms for a single exponential set, open shell calculation is the same as that for a closed shell calculation of the same order but using both spin functions.)

The improvement in the energy using the open-shell representation is quite clear, with the energy obtained at any value K approaching the value obtained at a value $K+1$ with the closed-shell representation with fixed exponents. In addition, the balance between the kinetic and potential components of the energy as reflected in the scale factor, shown in Table 4.1.2, also improves much more rapidly using the open-shell approach than by even the fixed-shell approach with two spin functions.

These gains might appear to be at a considerable cost in comparison with the improvement obtainable within the fixed-shell representation when the second spin function is used, since in the latter case the second spin function can be seen to provide a significant portion of the potential open-shell gain at virtually no cost, as no new radial integrals are required. This is, however, an unfair comparison in that

Table 4.1.3

(1s)²2s ²S Li Fermi Contact Term Using a Single Set of Exponential Parameters

Fixed closed-shell exponents ^a					Optimized open-shell exponents	
K	One spin function ^b		Two spin functions ^c		One spin function ^b	
	No. of Terms	$\langle 4\pi\delta(\vec{r}_i)\sigma_{z_i}\rangle$ (a ₀ ⁻³)	No. of Terms	$\langle 4\pi\delta(\vec{r}_i)\sigma_{z_i}\rangle$ (a ₀ ⁻³)	$\langle 4\pi\delta(\vec{r}_i)\sigma_{z_i}\rangle$ (a ₀ ⁻³)	
1	5	3.557 080 760 749	7		3.595 517 432 838	
2	18	4.558 993 859 096	28		2.778 3	
3	50	2.915 014 120 96	84	2.887 942	3.012 3	
4	120	3.008 230 204	210	2.902 746	2.923	
5	256	2.928 012	462		2.909	

a. $\alpha = \beta = 2.76$, $\gamma = 0.65$. b. Present workc. F. W. King and V. Shoup., Phys. Rev. A, 33, (1986) 2940

FIGURE 4.1.1 NON-LINEAR PARAMETERS USING A SINGLE EXPONENTIAL SET

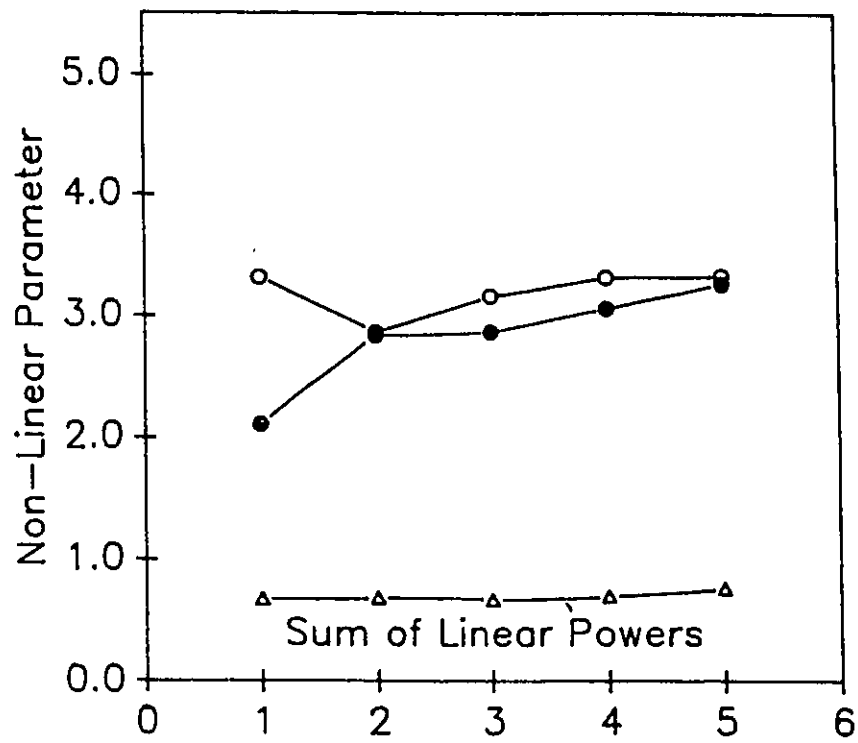


Table 4.1.4

Exponential Parameters for Single Set Calculation

	K = 1	2	3	4	5
α	3.31800	2.87057	3.16318	3.31933	3.32731
β	2.10280	2.84624	2.86873	3.06418	3.26378
γ	0.66597	0.67902	0.66410	0.69346	0.75678

a similar basis set enlargement is also available "for free" in the open-shell representation, although these results have not been calculated here.

Examination of the results for the Fermi contact term, shown in Table 4.1.3, display a similar improvement in convergence when the open-shell rather than the closed-shell representation is used. In this case, however, the closed-shell basis set with two spin functions offers substantially more flexibility in representing the form of the wavefunction at the origin than is possible with a single set of open-shell exponential parameters.

An interesting feature of both of these tables is the reduction in the numerical stability that appears to accompany the move from a closed- to an open-shell representation. This can best be appreciated by examining Figure 4.1.1 and Table 4.1.4, which show how the values of the "optimum" exponential parameters for the open-shell basis sets varied as the size of the basis set was increased to successive values of K . The word "optimum" is placed in quotation marks since the iterative optimization process was stopped for each value of K once it became apparent that further iterations at that order would produce insignificant improvement in the energy.

When the values of the "core" exponential parameters α and β are well separated, as for the exponential set at $K = 1$, the matrix elements exhibit numerical stability comparable to the corresponding closed-shell results, but when the values become very close the stability is reduced. This is especially noticeable in the cases $K = 2$ and 5. This reduction is attributed to the near linear dependence of terms with $i > j$ with the corresponding terms with $i < j$ that occurs when α and β are approximately equal.

The behaviour of the non-linear parameters as the size of the basis set is increased is much as one might anticipate for an "asymptotic" picture of the ground state. The values at $K = 1$ are very close to those obtained with very small basis

Table 4.1.5
(1s)²2s ²S Li Matrix Elements Using a Single Set of Exponential Parameters

Fixed closed-shell exponents ^a			Optimized open-shell exponents	
K	No. of Terms	$\langle r_i \rangle$ (a.u.)	No. of Terms	$\langle r_i \rangle$ (a.u.)
1	5	5.013 704 577 946 1	7	5.034 590 505 913 6
2	18	4.951 564 026 760 1	28	4.975 53
3	50	4.996 091 779 00	84	4.987 798 2
4	120	4.989 232 907 3	210	4.989 100 7
5	256	4.989 688 577	462	4.989 290
<hr/>				
K	No. of Terms	$\langle r_i^2 \rangle$ (10 ¹ a.u.)	No. of Terms	$\langle r_i^2 \rangle$ (10 ¹ a.u.)
1	5	1.887 626 223 760 0	7	1.880 686 299 839 3
2	18	1.790 949 047 114 8	28	1.815 51
3	50	1.843 152 431 24	84	1.832 919 2
4	120	1.834 642 533 7	210	1.834 576 9
5	256	1.835 619 47	462	1.835 124

a. $\alpha = \beta = 2.76$, $\gamma = 0.65$.

Table 4.1.6
(1s)²2s ²S Li Matrix Elements Using a Single Set of Exponential Parameters

Fixed closed-shell exponents ^a			Optimized open-shell exponents	
K	No. of Terms	$\langle r_i^3 \rangle$ (10 ¹ a.u.)	No. of Terms	$\langle r_i^3 \rangle$ (10 ¹ a.u.)
1	5	9.789 297 466 779	7	9.625 403 978 613
2	18	8.810 008 199 904	28	9.038 9
3	50	9.342 458 825 5	84	9.233 412
4	120	9.247 376 543	210	9.248 353
5	256	9.262 311 0	462	9.256 30
K	No. of Terms	$\langle r_i^{-1} \rangle$ (10 ¹ a.u.)	No. of Terms	$\langle r_i^{-1} \rangle$ (10 ¹ a.u.)
1	5	5.717 476 102 586 91	7	5.716 232 147 798 26
2	18	5.718 619 296 638 11	28	5.717 965
3	50	5.717 813 885 166	84	5.718 092 02
4	120	5.718 092 894 650	210	5.718 104 49
5	256	5.718 100 502 5	462	5.718 113

a. $\alpha = \beta = 2.76$, $\gamma = 0.65$.

Table 4.1.7
(1s)²2s ²S Li Matrix Elements Using a Single Set of Exponential Parameters

Fixed closed-shell exponents ^a			Optimized open-shell exponents	
K	No. of Terms	$\langle r_{ij} \rangle$ (a.u.)	No. of Terms	$\langle r_{ij} \rangle$ (a.u.)
1	5	8.740 090 125 679 8	7	8.759 909 624 29
2	18	8.597 074 951 142 0	28	8.642 0
3	50	8.681 394 413 00	84	8.665 083
4	120	8.667 843 042 9	210	8.667 586 5
5	256	8.668 731 71	462	8.667 938
<hr/>				
K	No. of Terms	$\langle r_{ij}^2 \rangle$ (10 ¹ a.u.)	No. of Terms	$\langle r_{ij}^2 \rangle$ (10 ¹ a.u.)
1	5	3.795 486 156 693 7	7	3.780 318 508 887 0
2	18	3.595 931 375 644 0	28	3.645 3
3	50	3.700 143 906 10	84	3.679 652
4	120	3.683 154 884 4	210	3.683 011
5	256	3.685 100 47	462	3.684 106

a. $\alpha = \beta = 2.76$, $\gamma = 0.65$.

Table 4.1.8
(1s)²2s ²S Li Matrix Elements Using a Single Set of Exponential Parameters

Fixed closed-shell exponents ^a			Optimized open-shell exponents	
K	No. of Terms	$\langle r_{ij}^{-1} \rangle$ (a.u.)	No. of Terms	$\langle r_{ij}^{-1} \rangle$ (a.u.)
1	5	2.246 756 030 332 2	7	2.216 684 794 858 44
2	18	2.206 567 444 255 47	28	2.199 32
3	50	2.197 864 248 718	84	2.198 408 84
4	120	2.198 300 800 175	210	2.198 244 34
5	256	2.198 226 963 5	462	2.198 231

K	No. of Terms	$\langle \delta(\vec{r}_i) \rangle$ (10 ¹ a.u.)	No. of Terms	$\langle \delta(\vec{r}_i) \rangle$ (10 ¹ a.u.)
1	5	1.295 992 628 203 02	7	1.362 704 261 237 57
2	18	1.363 847 149 984 78	28	1.380 1
3	50	1.381 017 176 272 4	84	1.383 137
4	120	1.382 892 240 26	210	1.384 20
5	256	1.383 611 190	462	1.384 119

a. $\alpha = \beta = 2.76$, $\gamma = 0.65$.

sets in early open-shell studies⁴⁴⁻⁴⁶ that did not explicitly incorporate powers of the interelectronic coordinates, and those at $K = 2$ are close to the values obtained by Larsson⁸ and by Perkins⁶³ with small correlated basis sets. The gradual increase in the parameters thereafter is consistent with the inclusion of higher powers of the radial coordinates r_i . The optimized non-linear parameter values were obtained by starting the calculation of the $K = 1$ set with all non-linear parameters set approximately equal to 3 to avoid introducing any subjective bias, and then adopting the best set of non-linear parameters (i.e. that set producing the lowest variational ground state energy) as the starting point for the optimization of the next larger size basis set. The process was repeated for each successive increase in basis set size.

For the purpose of comparison with other published results, the calculated values of some of the moments of r_i and r_{ij} with open and closed basis sets, as well as the electron density at the nucleus, are presented in Tables 4.1.5 through 4.1.8.

4.2 Calculations Using Six Exponential Sets

With the single exponential set results providing a more consistent set of benchmarks than previously published results, the merits of the multiple set method as implemented here may be objectively assessed. In the following subsections results for the same quantities treated in the preceding section will be presented. In each case, however, the convergence of the matrix elements will be examined and, where possible, the convergence pattern will be used to extrapolate computational error limits.

The optimization process in this case proceeded as for the single exponential set calculations up to order $K = 5$. The non-linear parameters for the basis sets

FIGURE 4.2.1 NON-LINEAR PARAMETERS USING SIX EXPONENTIAL SETS

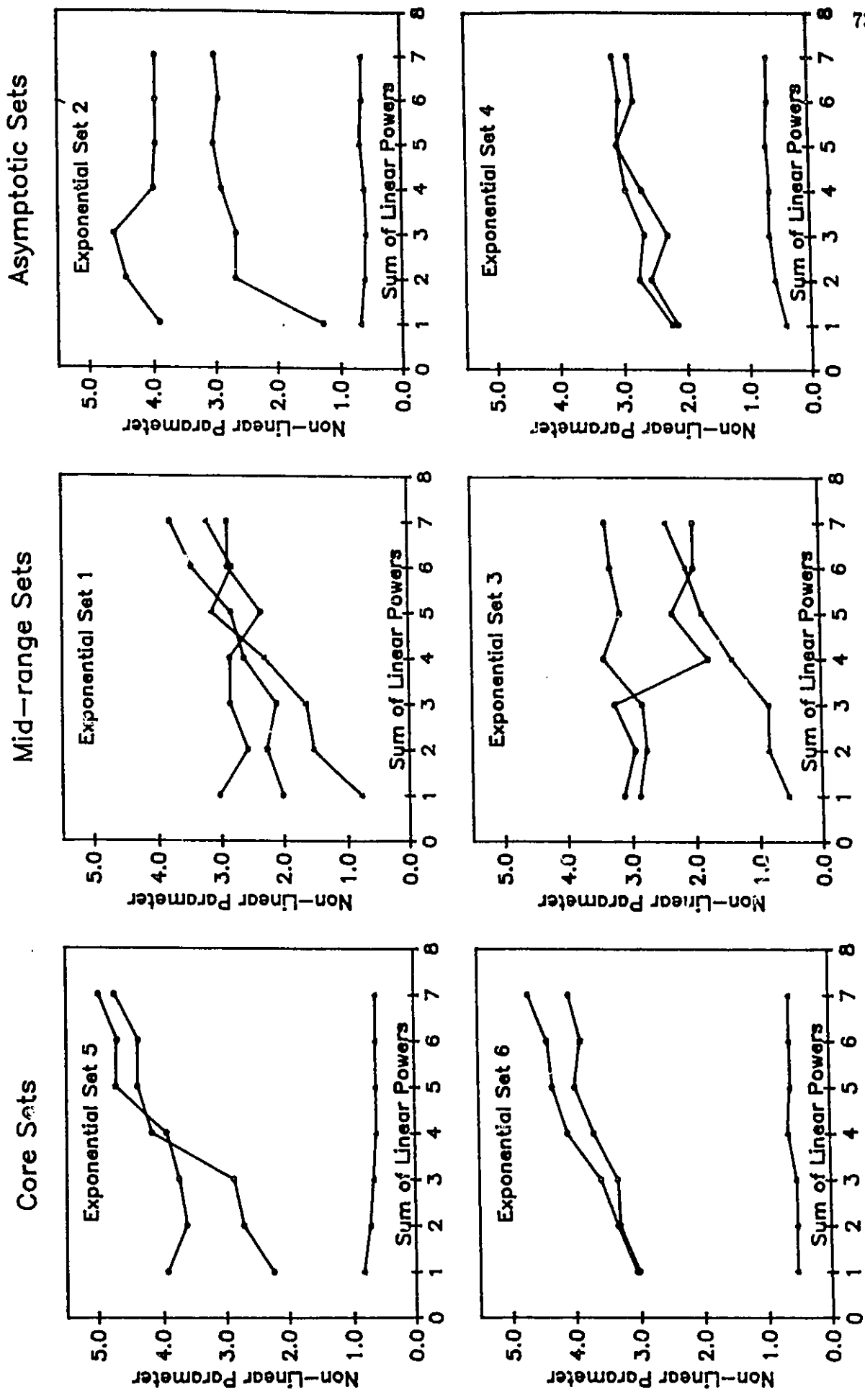


Table 4.2.1 "Optimum" Exponential Parameters for Six Set Calculation

Set \ K =	1	2	3	4	5	6	7
1	α	3.01671	2.56998	2.84922	2.85312	2.34525	2.88
	β	2.00433	2.25689	2.10362	2.62969	2.83157	3.46
	γ	0.77871	1.52080	1.63968	2.29353	3.13347	2.81
2	α	3.90313	4.43178	4.61039	3.98701	3.94747	3.95
	β	1.26206	2.67249	2.65361	2.88788	3.01528	2.92
	γ	0.67882	0.61402	0.58957	0.62014	0.68277	0.65
3	α	3.11493	2.93779	3.26155	1.78869	2.35023	2.00
	β	2.87440	2.76390	2.83701	3.42880	3.16554	3.31
	γ	0.53048	0.84201	0.84415	1.41139	1.87791	2.12
4	α	2.22497	2.73432	2.64710	2.93512	3.05970	3.02
	β	2.13445	2.54993	2.27288	2.68399	3.06623	2.79
	γ	0.40470	0.57423	0.65885	0.64608	0.69647	0.66
5	α	3.92740	3.62826	3.75133	3.94170	4.72668	4.70
	β	2.23750	2.72137	2.87328	4.16875	4.39029	4.37
	γ	0.83330	0.72684	0.67400	0.62775	0.63246	0.63
6	α	3.04984	3.34350	3.600849	4.11071	4.35485	4.43
	β	3.01193	3.30923	3.34331	3.71149	3.98920	3.89
	γ	0.53333	0.53333	0.54199	0.66890	0.62579	0.64

Table 4.2.2

(1s)²2s ²S state of Li Using Six Sets of Exponential Parameters

Scale Factor

K	No. of Terms	$\eta - 1$
1	18	8.35 [-5]
2	48	6.41 [-6]
3	108	1.80 [-6]
4	216	1.77 [-7]
5	396	4.81 [-8]
6	690	2.06 [-8]
7	1134	4.26 [-9]

Table 4.2.3

(1s)²2s ²S state of Li Using Six Sets of Exponential Parameters

Convergence of Nonrelativistic Eigenvalues

K	No. of Terms	Energy (a.u.)	Difference in Energies	Ratio of Differences
1	18	-7.476 946 306 762		
2	48	-7.477 866 720 377 8	-0.000 920 413 626	
3	108	-7.478 041 912 521	-0.000 175 192 133	5.25
4	216	-7.478 058 843 95	-0.000 016 931 43	10.35
5	396	-7.478 060 126 5	-0.000 001 282 5	13.20
6	690	-7.478 060 266 1	-0.000 000 139 6	9.19
7	1134	-7.478 060 312	-0.000 000 046	3.0

Extrapolation: -7.478 060 326 (10)

with $K = 6$ and $K = 7$ seven were determined by extrapolation from the results up to $K = 5$. The final values for these sets are shown in Figure 4.2.1 and Table 4.2.1.. Note that the extrapolated non-linear exponential parameters used at $K = 6$ and at $K = 7$ were based upon an earlier series of calculations in which the results at orders four and five were less fully optimized. As explained earlier, as long as these parameters remain fairly close to the optimum values, the deviations from the absolute energy minimum at any order is small in comparison with the improvement possible by increasing the basis set size to the next order. That no serious compromise has been made in this case may be seen by examining the behaviour of both the scale factors and the non-relativistic energies. Neither set of values changes its trend in any marked way at the transition to extrapolated parameter values. The scale factors are given in Table 4.2.2..

Although the need to stop the optimization process at $K = 5$ for the six-set non-linear exponential parameters makes the interpretation of the graphs shown in Figure 4.2.1 more difficult, the *ad hoc* partitions used to assist in keeping the basis set sizes small appear to have performed as expected, differentiating themselves naturally into sets adapted to descriptions of the core, mid-range, and asymptotic distance regions.

4.2.1 Nonrelativistic Ground State Energy E_{nr}

The nonrelativistic energy results are presented in Table 4.2.3.. Comparison with the results for the first five orders of single exponential set open-shell energy values in Table 4.1.1 shows the six-set results when K equals one and two are close to the single set results one order higher, and for values of $K > 2$ they surpass these single set results, gaining thereby nearly two orders in K over the single set (fixed)

closed-shell results. This would suggest that, for example, the six-set $K = 4$ result should be about equivalent to a full $K = 6$ single set closed-shell calculation, and therefore surpass (cf. Table 3.1) both the 251- and 352-term results of King and Shoup⁹ (-7.478056 and -7.478058 a.u., respectively), as it does. In fact, this 216-term six-set result is on a comparable level of accuracy to the 602-term single set closed-shell calculation of King¹⁰ (-7.478059 a.u.), and the much more elaborate 246-term open-shell calculation¹² of King and Bergsbaken ($-7.478\ 059\ 008$ a.u.). The latter value represents an intermediate stage in their calculation, which resulted, using a 296-term wavefunction, in the best previously published variational upper bound to the nonrelativistic ground state energy of lithium, at $-7.478\ 059\ 528$ a.u..

The multiple basis set method as employed in the present study, with six sets, improves upon that result at the very next order, with $K = 5$ and 396 terms in the basis set. The best value for the variational upper bound to the ground state energy of lithium, obtained in the current study at order $K = 7$ with a basis set of 1134 terms, is $-7.478\ 060\ 312$ a.u.. This represents an improvement of two orders of magnitude in accuracy over previous calculations. In addition, it is possible to use the series of ratios of successive differences in the energy eigenvalue to construct computational error limits on the extrapolated limit of this energy value as the size of the basis set is made arbitrarily large. This is done by regarding the successive energy differences as terms in a geometric series. Using first a large and then a small ratio of terms, we place the extrapolated limit at $-7.478\ 060\ 326$ (10) atomic units of energy.

This result is in agreement with the semi-empirical estimate of E_{nr} , -7.478060 a.u., given in the introduction and allows for more precise comparison with experiment of the total relativistic, QED and mass polarization contributions to the ground state energy. At present the least accurately calculated of these values is

the Breit interaction, although the deviation of the matrix element of the delta function (13.84 a.u.) given in Table 4.2.12 from the corresponding value for the $1s^2$ 1S state of Li^+ (13.70 a.u.⁴) suggests that the Lamb shift value cited in Table 1.2 may also be in error by up to one percent.

Before leaving this section, it is worth examining the methodology of King and Bergsbaken, which represents a more radical departure from previous closed-shell calculations than the multiple basis set method employed here. Their single-spin-function calculation involved building up the wavefunction term by term, optimizing the orbital exponents of each new term as it was added to the basis set, and then keeping these parameters fixed thereafter as subsequent terms were added. Although the final set selected could, if desired, be iteratively re-optimized in the same term by term fashion, starting over at the first term, these authors found little change after the second pass on just the first five terms and terminated the optimization process at that point. While this procedure offers, in principle, greater flexibility in the wavefunction than the multiple basis set method, it does not appear to offer any significant size advantage for the basis set and possesses a few serious disadvantages.

First, there is less opportunity to save and re-cycle integrals with a common set of non-linear exponential parameters, making this appear to be a relatively expensive computational approach, even compared with the present six-set calculations.

Second, without subsequent iterative optimization passes through the set of basis set terms, it is much harder for terms added late in the sequence to compensate for the shortcomings already "locked-in" by fixing the non-linear parameters of earlier terms. Such a sequential approach to the optimization process was, in fact, tried in a preliminary attempt at optimizing the six-set calculation of the present study, but was found to be more time-consuming than the simultaneous

optimization of all six exponential parameter sets.

Third, the selection of linear powers of r_1 and r_{ij} involves, as the authors point out, "a good deal of trial and error", and thus retains a key weakness of earlier studies using Hylleraas type wavefunctions. Term selection using this method is even more subjective than in previous closed-shell calculations using a single set of fixed exponential parameters, as King and Bergsbaken found it worthwhile to include "several repetitions of key terms" with different exponents.

Fourth, and most important, it is difficult to attach a physical interpretation to such a basis set, which appears to abandon the physically useful idea of "shells" entirely. In light of the early work of James and Coolidge establishing the retained separate identities of the core and the valence orbital for the lithium ground state, this seems particularly undesirable. Furthermore, it is unclear how one would approach the problem of performing a calculation for an excited state of the same symmetry using this method.

The multiple basis set method, in contrast, adopts the use of additional sets of nonlinear exponential parameters in a way that supplements in a clear fashion the usual notion of shells, and is readily extended (at least in the case of two-electron systems) to calculations involving excited states.

4.2.2 The Fermi Contact Term

Table 4.2.4 shows the results of calculations of the Fermi contact term as the basis set is enlarged.

The convergence by order $K = 5$ to the value 2.906 a_0^{-3} (to four significant figures) is in agreement with a number of earlier calculations which used two spin functions. This result tends to support the hypothesis that the use of the second

Table 4.2.4

(1s)²2s ²S state of Li Using Six Sets of Exponential ParametersConvergence of $\langle 4\pi \delta(\vec{r}_i) \sigma_{z_i} \rangle$

K	No. of Terms	$\langle 4\pi \delta(\vec{r}_i) \sigma_{z_i} \rangle$ (a ₀ ⁻³)	Difference in $\langle 4\pi \delta(\vec{r}_i) \sigma_{z_i} \rangle$	Ratio of Differences
1	18	2.765 299 665		
2	48	2.996 113 143 59	+0.230 813 478	
3	108	2.914 905 05	-0.081 208 09	2.84
4	216	2.908 233 5	-0.006 671 6	12.17
5	396	2.905 65	-0.002 58	2.59
6	690	2.905 7	+0.000 0	-
7	1134	2.906 04	+0.000 3	-

Extrapolation: 2.9060 (3)

spin function is not critical to the calculation of this matrix element. The slow convergence as K is increased from 5 to 7, due partly to the use of extrapolation rather than optimization to determine the non-linear exponential parameters at orders 6 and 7, leaves room for further study of this point.

In this regard, the sensitivity of the Fermi contact term to small changes in the wavefunction deserves to be highlighted in the spirit of Bunge's discussion²⁰ of the need for high numerical accuracy in such calculations. By way of example, the extended optimization of the $K = 5$ basis set reduced the energy eigenvalue by slightly less than 1 part in 10^8 , but in so doing the value of f changed from 2.9053 to 2.9057 a_0^{-3} , a change of approximately 1 part in 10^4 . This reflects the fact that the energy is stationary with respect to first order variations in the wavefunction, while matrix elements of other operators not incorporated directly in the variational principle are not. To achieve a precision of 1 part in 10^5 in f , we thus expect to demand a precision of at least 1 part in 10^{10} in the variational ground state energy. From our experience with the energy convergence shown in Table 4.2.3, this level of accuracy will only be achieved with a calculation of approximately order $K = 8$ or 9.

Thus, the need for a cautious approach to any published calculated value of this term, including the present calculation, is one of the clearest results of this study.

In particular the close agreement with experiment of the result of King and Bergsbaken, who obtained a value of 2.90637 a_0^{-3} (corrected for the effects of finite nuclear mass), appears in light of the present slow convergence to be fortuitous. If the extrapolated energy limit of $-7.478060326 \text{ a.u.}$ is accurate, then the inherent uncertainty in their value of f is approximately 0.001 a_0^{-3} . The larger fluctuations that these authors found in the values of f as the size of the basis set was enlarged in comparison to those observed in previous calculations using both spin functions is also understandable in terms of this type of reasoning, as the calculations using two

spin functions improve the energy very little in comparison with the impact on the Fermi contact term. Thus the fluctuations would be expected to be smaller in such calculations where there is a clear emphasis on improving the latter values.

Applying the same estimation method to the results of this study, the inherent error in f should be approximately 0.0001 a_0^{-3} . The more conservative computational error limit of $\pm 3 \times 10^{-4} \text{ a}_0^{-3}$ shown in Table 4.2.4 was obtained by treating the final value obtained at $K = 7$ as though it were the result for $K = 6$ and extrapolating the magnitude of the series of successive differences in the value of f .

The final value obtained in this work, $2.9060 (3) \text{ a}_0^{-3}$, must still be adjusted to take into account several corrections before it may be compared with the experimental value. The first of these corrections, which accounts for the effect of finite nuclear mass, reduces the calculated value by a factor

$$(1 + m_e/M_{Li})^{-3} = 0.9997654.$$

The value of f incorporating only this correction, as is sometimes reported in the literature^{9,10,12}, is $2.9054 (3) \text{ a}_0^{-3}$. This is less than the experimental value of $2.9061(3) \text{ a}_0^{-3}$ by an amount that would change the observed hyperfine splitting by approximately 200 KHz. Even with the earlier caution about convergence in mind it seems unlikely that the difference between these values could be reconciled with a more precise calculation.

There are, however, several other important corrections⁹¹ that must be considered before a valid comparison with experiment can be made. These include a correction C_{rel} to account for the use of nonrelativistic instead of Dirac wavefunctions in evaluating the matrix element of the delta function, a QED correction C_{qed} to account for the fact that the nuclear magnetic dipole is not a

point dipole, but is distributed over the nuclear volume, and smaller corrections to account for nuclear recoil and structure.

For hydrogen-like atoms, the relativistic correction factors for the $1^2S_{\frac{1}{2}}$ and $2^2S_{\frac{1}{2}}$ levels, are

$$C_{\text{rel}} = \begin{cases} 1 + \frac{3}{2}a^2Z^2 + \mathcal{O}(a^4) & \text{for } 1^2S_{\frac{1}{2}} \simeq 1.00072 \text{ for } Z = 3.0 \\ 1 + \frac{17}{8}a^2Z^2 + \mathcal{O}(a^4) & \text{for } 2^2S_{\frac{1}{2}} \simeq 1.00006 \text{ for } Z = 0.7 \end{cases}$$

while the QED correction factor is

$$C_{\text{qed}} = 1 - \frac{1}{2}Za^2(5 - 2 \ln 2) \simeq \begin{cases} 0.999711 & \text{for } Z = 3.0 \\ 0.999933 & \text{for } Z = 0.7 \end{cases}$$

Applying these corrections as though we had performed a non-relativistic independent-particle calculation gives a combined correction factor for the three-orbital product function of

$$C_{\text{rel}} \times C_{\text{qed}} = 1.00085 \quad (1.00063 \text{ if } Z = 3 \text{ is assumed for all QED corrections}).$$

We would expect this value to be smaller for the nonseparable wavefunction actually used. Nuclear recoil and structure corrections are expected to be smaller in magnitude, adding at most a few parts in 10^4 to the combined correction factor above.

For comparison, Lindgren¹⁴ calculated relativistic and finite size corrections assuming a homogeneous nuclear charge density, but pointlike nuclear moments,

that increased his calculated value of the hyperfine parameter by a factor

$$C_{\text{Lindgren}} = 1.00057 .$$

If the QED correction is applied assuming $Z = 3$, the combined correction would be

$$C_{\text{Lindgren}} \times C_{\text{qed}} = 1.00035 .$$

Using this value as an estimate of the true corrections required, our calculated result for the Fermi contact term becomes 2 9064 (3) a.u., in closer agreement with the experimental value of 2.9061 (3) a.u.. While this result is somewhat speculative, the above discussion indicates that the relativistic, QED and finite nuclear size corrections can be expected to shift the value obtained in the present calculation of the Fermi contact interaction in the right direction to improve the agreement with experiment.

4.2.3 Matrix Elements of Other Operators

The matrix elements of the moments of r_i and r_{ij} , and of the electron density at the nucleus, are presented in Tables 4.2.5 through 4.2.12.

The convergence of these matrix elements is non-monotonic in all cases except for matrix elements of r_i^{-1} and r_{ij}^{-1} , which converge monotonically, along with the energy. In all cases except for the electron density at the nucleus, convergence has been achieved to one or two more significant figures than previously available in the literature.

Table 4.2.5

(1s)²2s ²S state of Li Using Six Sets of Exponential Parameters

Convergence of $\langle r_i \rangle$

K	No. of Terms	$\langle r_i \rangle$ (a.u.)	Difference in $\langle r_i \rangle$	Ratio of Differences
1	18	5.002 389 254 05		
2	48	4.990 508 488 678	-0.011 880 765 37	
3	108	4.989 663 089 63	-0.000 845 399 05	14.05
4	216	4.989 515 848	-0.000 147 242	5.74
5	396	4.989 523 7	+0.000 007 9	18.6
6	690	4.989 523 2	-0.000 000 5	15.8
7	1134	4.989 523 3	+0.000 000 1	5.

Extrapolation: 4.989 523 3 (1)

Table 4.2.6

(1s)²2s ²S state of Li Using Six Sets of Exponential ParametersConvergence of $\langle r_i^2 \rangle$

K	No. of Terms	$\langle r_i^2 \rangle$ (10 ⁴ a.u.)	Difference in $\langle r_i^2 \rangle$	Ratio of Differences
1	18	1.851 192 537 77		
2	48	1.836 524 701 98 9	-0.014 667 835 78	
3	108	1.835 591 553 91	-0.000 933 148 08	15.72
4	216	1.835 442 224	-0.000 149 330	6.25
5	396	1.835 460 4	+0.000 018 2	5.13
6	690	1.835 461	+0.000 001	18.
7	1134	1.835 462	+0.000 001	1.

Extrapolation: 1.835 462 (1)

Table 4.2.7

(1s)²2s ²S state of Li Using Six Sets of Exponential ParametersConvergence of $\langle r_i^3 \rangle$

K	No. of Terms	$\langle r_i^3 \rangle$ (10 ⁴ a.u.)	Difference in $\langle r_i^3 \rangle$	Ratio of Differences
1	18	9.426 543 038 3		
2	48	9.268 703 000 62	-0.157 840 037 7	
3	108	9.261 176 853 4	-0.007 526 147 2	20.97
4	216	9.259 902 6	-0.001 274 3	5.91
5	396	9.260 183	+0.000 280	45.5
6	690	9.260 21	+0.000 03	9.3
7	1134	9.260 22	+0.000 01	3.

Extrapolation: 9.260 22 (1)

Table 4.2.8

 $(1s)^2 2s \ ^2S$ state of Li Using Six Sets of Exponential ParametersConvergence of $\langle 1 / r_i \rangle$

K	No. of Terms	$\langle 1 / r_i \rangle$ (a.u.)	Difference in $\langle 1 / r_i \rangle$	Ratio of Differences
1	18	5.717 538 090 71		
2	48	5.718 069 028 068 0	+0.000 530 937 36	
3	108	5.718 103 670 127	+0.000 034 642 059	15.33
4	216	5.718 110 450 5	+0.000 006 780 4	5.11
5	396	5.718 110 804 3	+0.000 000 353 8	19.16
6	690	5.718 110 8	+0.000 000 0	-
7	1134	5.718 110 9	+0.000 000 1	-

Extrapolation: 5.718 110 9 (1)

Table 4.2.9

(1s)²2s ²S state of Li Using Six Sets of Exponential ParametersConvergence of $\langle r_{ij} \rangle$

K	No. of Terms	$\langle r_{ij} \rangle$ (a.u.)	Difference in $\langle r_{ij} \rangle$	Ratio of Differences
1	18	8.694 661 806 64		
2	48	8.670 421 581 71	-0.024 240 224 93	
3	108	8.668 691 753 93	-0.001 729 827 78	14.01
4	216	8.668 383 70	-0.000 308 05	5.62
5	396	8.668 398 1	+0.000 014 4	21.4
6	690	8.668 397	-0.000 001	14.
7	1134	8.668 397	+0.000 000	-

Extrapolation: 8.668 397 (1)

Table 4.2.10

(1s)²2s ²S state of Li Using Six Sets of Exponential ParametersConvergence of $\langle r_{ij}^2 \rangle$

K	No. of Terms	$\langle r_{ij}^2 \rangle$ (10 ¹ a.u.)	Difference in $\langle r_{ij}^2 \rangle$	Ratio of Differences
1	18	3.716 330 633 69		
2	48	3.686 970 846 42	-0.029 359 787 27	
3	108	3.685 066 519 62	-0.001 904 326 80	15.42
4	216	3.684 746 2	-0.000 320 3	5.95
5	396	3.684 781 8	+0.000 035 6	9.00
6	690	3.684 783	+0.000 001	36.
7	1134	3.684 784	+0.000 001	1.

Extrapolation: 3.684 784 (1)

Table 4.2.11

(1s)²2s ²S state of Li Using Six Sets of Exponential ParametersConvergence of $\langle 1 / r_{ij} \rangle$

K	No. of Terms	$\langle 1 / r_{ij} \rangle$ (a.u.)	Difference in $\langle 1 / r_{ij} \rangle$	Ratio of Differences
1	18	2.198 721 554 421		
2	48	2.198 273 642 833 51	-0.000 447 911 587	
3	108	2.198 227 185 289 6	-0.000 046 457 543	9.64
4	216	2.198 213 664 7	-0.000 013 520 5	3.44
5	396	2.198 212 160	-0.000 001 505	8.98
6	690	2.198 212 06	-0.000 000 10	15.1
7	1134	2.198 212 00	-0.000 000 06	1.7

Extrapolation: 2.198 212 00 (5)

Table 4.2.12

(1s)²2s ²S state of Li Using Six Sets of Exponential ParametersConvergence of $\langle \delta(\vec{r}_i) \rangle$

K	No. of Terms	$\langle \delta(\vec{r}_i) \rangle$ (10 ⁴ a.u.)	Difference in $\langle \delta(\vec{r}_i) \rangle$	Ratio of Differences
1	18	1.386 136 497 05		
2	48	1.383 115 323 678	-0.003 021 173 37	
3	108	1.384 698 236 4	+0.001 582 912 7	1.91
4	216	1.384 316 59	-0.000 381 65	4.15
5	396	1.384 255	-0.000 061	6.26
6	690	1.384 27	+0.000 01	6.
7	1134	1.384 26	-0.000 01	1.

Extrapolation: 1.384 26 (1)

5. CONCLUSIONS

The multiple basis set method has proven to be a valuable tool in variational calculations of the ground state of lithium using Hylleraas type basis sets, improving the accuracy to which the upper bound to the non-relativistic ground state energy is known by two orders of magnitude over previously published values. The value obtained for this variational upper bound, $-7.478\,060\,312$ a.u., and the extrapolated convergence limit, $-7.478\,060\,326(10)$ a.u., are in agreement with the semi-empirical estimate of the non-relativistic ground state energy, $-7.478\,060$ a.u., given in Table 1.2 of the introduction. Note that all of the estimates discussed in the introduction rely heavily upon high precision one- and two-electron calculations, including in particular values for the Lamb shift that are appropriate for a two-electron system. There is a strong need for a multielectron treatment of the relativistic and QED corrections, as Seely⁹² has recently emphasized in connection with the relativistic MBPT calculations¹⁷ of Johnson et al..

The value obtained for the Fermi contact term has converged to slightly better than four figures to a value $2.9054(3) a_0^{-3}$, which lies $0.0007(6) a_0^{-3}$ below the experimental value, $2.9061(3) a_0^{-3}$, before corrections for relativistic, QED and finite nuclear size effects. The slow convergence observed serves to emphasize the need for care in using calculated values of this parameter found in the literature. We believe that the error limits quoted for this value portray the best accuracy that may be expected of any such calculations made to date. In addition, despite the slow convergence observed for the Fermi contact term, the initial assumption that the use of the second spin function would be unnecessary with the use of multiple sets of basis set terms having different non-linear exponential parameters appears to be justified.

The precision to which the calculated matrix elements of the moments of the electron-nucleus separation r_i and the interelectron separation r_{ij} , and of the electron density at the nucleus, are known have been improved by one or two significant figures.

These accuracy gains are made with a much smaller basis set than would have been required for a closed-shell calculation with fixed non-linear exponential parameters. If the rule of thumb of section 4.2.1, that a six-set calculation of order K is comparable to a single set calculation with fixed exponents of order $K+2$, holds, then considerably more than twice as large a basis set (perhaps even four times as large) would have been required to achieve comparable accuracy with the latter. This presumes that the inevitable numerical problems associated with very large basis sets would still be manageable. Already with our 1134 term basis set it is clear that we are very near the limit of numerical precision possible with the current computer hardware using double precision (16 figure) arithmetic, so it is certain that such a calculation would require much more sizable computing resources with multiple precision arithmetic capability.

Even the extension of the present calculation to order $K = 8$ or 9 , which would be useful in reducing the the computational error limits upon the calculated value of the hyperfine splitting, may not be possible without such resources.

6. SUGGESTIONS FOR FUTURE WORK

The present work lends itself to explorations in many different directions. While the immediate extensions to higher K shells which would allow a more precise calculation of the hyperfine splitting of the ground state may be dependent upon the availability of large scale computing resources, many other calculations are within reach of present computing capabilities. For example, another sensitive test of the quality of the variational wavefunctions, but emphasizing a different region of configuration space than the Hamiltonian, is the determination of oscillator strengths.

In particular the resonance transition for lithium deserves attention. This transition has been the subject of considerable theoretical interest, but agreement with experiment⁹³ has remained elusive. Indeed, Blundell et al.¹⁵ suggest that, in light of the agreement between their own MBPT calculation, the MCHF results of Froese-Foscher⁹⁴ and the calculation of Sims et al.⁹⁵, that the discrepancy is likely to be due to experimental causes. All theoretical calculations to date have used wave functions, however, that are almost certainly of lesser quality than those obtained in the present study. A similar calculation for the $2^2P_{\frac{1}{2}}$ state will enable a more sensitive theoretical comparison with the experimental result for the resonance lifetime to be made.

High precision calculations and measurements of resonance wavelengths for members of the lithium isoelectronic sequence are also of interest from the perspective of enabling sensitive tests of one-electron QED effects to be made. The important role that accurate wavelength measurements could play in this regard was highlighted by Berry et al.⁹⁶ a decade ago. At the same time, they emphasized the need for a more consistent relativistic theory of many electron

atoms beyond perturbation approaches using the Bethe-Salpeter equation. Recent results from tokamak experiments⁹⁷ examining lithiumlike resonances in elements with $Z = 22 - 42$ and relativistic MBPT calculations^{16,17} have shown that differences between theory and experiment for the $2p_{1/2} - 2s_{1/2}$ resonance energies and the $2p_{3/2} - 2p_{1/2}$ fine structure splittings may be reconciled using a screened one-electron Lamb-shift. However the differences in the resonance energies for the first few members of the isoelectronic sequence are larger than the unscreened one-electron Lamb shifts and so this cannot explain these discrepancies. Independent calculations using Hylleraas-type wavefunctions, which account for complex electron correlation effects quite differently, would be valuable in exploring this problem. This further underscores the need for incorporating relativistic and radiative corrections in a major extension of the present work.

More immediately accessible, however, are calculations of a number of excited states of lithium, including doubly excited states. These should be especially attractive candidates for study with the multiple basis set method as the natural distance scales are more distinct than for the ground state. Already, very significant accuracy improvements have been achieved using the doubled basis set method in highly excited two-electron systems.

Finally, all the above calculations may be extended to include higher Z members of the lithium isoelectronic sequence.

APPENDIX 1

Calculation of Subsidiary Integrals

This appendix will outline the calculation of the integral

$$W(l, m, n; a, \beta, \gamma) = \int_0^{\infty} dx x^l e^{-ax} \int_x^{\infty} dy y^m e^{-\beta y} \int_y^{\infty} dz z^n e^{-\gamma z}, \quad (\text{A1-1})$$

and two other subsidiary integrals,

$$V(l, m; a, \beta) = \int_0^{\infty} dx x^l e^{-ax} \int_x^{\infty} dy y^m e^{-\beta y} \quad (\text{A1-2})$$

and

$$A(l; a) = \int_0^{\infty} dx x^l e^{-ax} \quad (\text{A1-3})$$

for values of the linear powers such that $l \geq 0$, $l + m \geq -1$ and $l + m + n \geq -2$.

Although a number of recursion relations exist for these integrals³⁴, their use requires caution as severe loss of accuracy can result due to numerical cancellations.

The following integral, evaluated using integration by parts, is useful in evaluating these integrals when the powers l , m and n in the expressions above are all non-negative:

$$\int_p^{\infty} dr r^n \exp(-ar) = \sum_{j=0}^n \frac{n!}{j!} \frac{p^j \exp(-ap)}{a^{n+1-j}}, \quad n \geq 0. \quad (\text{A1-4a})$$

The A integral may be evaluated directly using this result to obtain

$$A(l; a) = \int_0^{\infty} dx x^l e^{-ax} = \frac{l!}{a^{l+1}}, \quad l \geq 0. \quad (\text{A1-3.1})$$

The V integral for $l, m \geq 0$ uses the same expression twice to obtain

$$\begin{aligned} V(l, m; a, \beta) &= \sum_{j=0}^m \frac{m!}{j!} \frac{1}{\beta^{m+1-j}} \int_0^{\infty} dx x^{l+j} e^{-(a+\beta)x} \\ &= \sum_{j=0}^m \frac{m!}{j!} \frac{1}{\beta^{m+1-j}} A(l+j; a+\beta). \end{aligned} \quad (\text{A1-2.1})$$

The expression corresponding to (A1-4a) with a negative power of r in the integrand is

$$\begin{aligned} \int_p^{\infty} r^{-n} \exp(-ar) &= - \sum_{j=1}^{n-1} (-1)^j \frac{(n-1-j)!}{(n-1)!} a^{j-1} \frac{\exp(-ap)}{p^{n-j}} \\ &\quad + \frac{(-a)^{n-1}}{(n-1)!} Ei(-ap), \quad n \geq 1, \end{aligned} \quad (\text{A1-4b})$$

with the summation in the last equation appearing only for $n \geq 2$ and with the definition of the exponential integral given by

$$Ei(-ax) = - \int_{ax}^{\infty} \frac{\exp(-t)}{t} dt = - \int_x^{\infty} \frac{\exp(-at)}{t} dt, \quad (\text{A1-4c})$$

with a and x both greater than zero. Expression (A1-4b), which includes an alternating series, leads to problems with numerical cancellation. Furthermore,

while this expression leads to V integrals with $l \geq 0$ and m negative which incorporate the integral

$$I(l; a, \beta) \doteq \int_0^{\infty} dx x^l \exp(-ax) Ei(-\beta x),$$

which is expressible in terms of a hypergeometric function as

$$I(l; a, \beta) = - \frac{l!}{(l+1)(a+\beta)^{l+1}} {}_2F_1(1, l+1; l+2; \frac{a}{a+\beta}),$$

when it is applied to the case of W integrals with l and m non-negative but $n < 0$, the related but more difficult semi-definite integral

$$J_{-1}(x; \beta, \gamma) \doteq \int_x^{\infty} dy y^{-1} \exp(-\beta y) Ei(-\gamma y),$$

arises. An workable approach along these lines could not be found.

Instead, for the V integral with $l \geq 0$ and $m < 0$, the approach adopted was that used by Öhrn and Nordling⁵³, which is based upon the use of the recursion relation³⁴.

$$V(l, -m; a, \beta) = \frac{1}{l+1} \left\{ a V(l+1, -m; a, \beta) + A(l+1-m; a+\beta) \right\} \quad (A1-2.2)$$

Applying this relation recursively, the following expression is obtained:

$$V(l, -m; a, \beta) = \sum_{j=1}^N \frac{a^{j-1} l!}{(l+j)!} A(l+j-m; a+\beta) + \frac{a^N l!}{(l+N)!} V(l+N, -m; a, \beta). \quad (A1-2.3)$$

But note that

$$\begin{aligned}
 V(l, -m; a, \beta) &= \int_0^\infty dx x^l e^{-ax} \int_x^\infty dy y^{-m} e^{-\beta y} \\
 &= \int_0^\infty dx x^{l-m} e^{-ax} \int_x^\infty dy \left[\frac{x}{y} \right]^m e^{-\beta y} \\
 &< \int_0^\infty dx x^{l-m} e^{-ax} \int_x^\infty dy [1] e^{-\beta y} = \frac{1}{\beta} \int_0^\infty dx x^{l-m} e^{-(a+\beta)x} \\
 &= \frac{1}{\beta} A(l-m; a+\beta) = \frac{1}{\beta} \frac{(l-m)!}{(a+\beta)^{l-m+1}} \quad (A1-2.4)
 \end{aligned}$$

So the remainder term in equation (A1-2.3) after N iterations of the recursion relation, which we shall denote by $R_V(N; l, -m; a, \beta)$, is seen to be

$$\begin{aligned}
 R_V(N, l, -m; a, \beta) &= \frac{a^N l!}{(l+N)!} V(l+N, -m; a, \beta) \quad (A1-2.5) \\
 &< \frac{a^N l!}{\beta} \frac{(l+N-m)!}{(l+N)!} \frac{1}{(a+\beta)^{l+N-m+1}}
 \end{aligned}$$

Defining $l_{(-m)} \doteq \frac{(l-m)!}{l!} = \frac{1}{l(l-1) \dots (l-m+1)},$

valid for $l \geq m$, the bound on the remainder may be expressed as

$$R_V(l, -m, N; a, \beta) < \frac{l!}{\beta(a+\beta)^{l-m+1}} (l+N)_{-m} \left[\frac{a}{a+\beta} \right]^N. \quad (A1-2.6)$$

Adopting the notation "+<" to mean, exactly as it reads, "plus an amount less than", the expression for $V(l, -m; a, \beta)$ may be written

$$V(l, -m; a, \beta) = \sum_{j=1}^N \frac{a^{j-1} l!}{(l+j)!} A(l+j-m; a+\beta) + < \frac{a^N l!}{\beta(l+N)!} A(l+N-m; a+\beta), \quad (\text{A1-2.7})$$

or, expanding the A -integrals as above and extracting a common factor, as

$$V(l, -m; a, \beta) = \frac{l!}{a(a+\beta)^{l-m+1}} \left\{ \sum_{j=1}^N \left[\frac{a}{a+\beta} \right]^j (l+j)_{-m} + < \frac{a}{\beta} \left[\frac{a}{a+\beta} \right]^N (l+N)_{-m} \right\}.$$

Note that as each term in this series is smaller than the corresponding term in the infinite series for the logarithm,

$$\ln \left[\frac{a+\beta}{a} \right] = \sum_{j=1}^{\infty} \left[\frac{a}{a+\beta} \right]^j \frac{1}{j} = \sum_{j=1}^{\infty} \left[\frac{a}{a+\beta} \right]^j (j)_{-1}, \quad (\text{A1-8})$$

the series for $V(l, -m; a, \beta)$ converges faster than the logarithm as N tends to infinity (except, of course for the case $V(0, -1; a, \beta) = \frac{1}{a} \ln \left[\frac{a+\beta}{a} \right]$).

If the multiplicative factor in the series for $V(l, -m; a, \beta)$ is re-expressed as

$$\begin{aligned} \frac{l!}{a(a+\beta)^{l-m+1}} &= A(l-m+1; a+\beta) \left[\frac{a+\beta}{a} \right] \frac{l!}{(l-m+1)!} \\ &= \frac{A(l-m+1; a+\beta)}{(l+1)} \left[\frac{a+\beta}{a} \right] \frac{(l+1)!}{(l+1-m)!} \\ &= \frac{A(l-m+1; a+\beta)}{(l+1)} \left[\frac{a+\beta}{a} \right] \frac{1}{(l+1)_{-m}}, \end{aligned}$$

the series may be written as

$$V(l, -m; a, \beta) = \frac{A(l-m+1; a+\beta)}{(l+1)} \left[\frac{a+\beta}{a} \right] \left\{ \sum_{j=1}^N \left[\frac{a}{a+\beta} \right]^j \frac{(l+j)_{-m}}{(l+1)_{-m}} \right. \\ \left. + \frac{a}{\beta} \left[\frac{a}{a+\beta} \right]^N \frac{(l+N)_{-m}}{(l+1)_{-m}} \right\}. \quad (\text{A1-2.8})$$

Noting that

$$\frac{(l+j)_{-m}}{(l+1)_{-m}} = \frac{(l+1)}{(l+j)} \frac{l}{(l+j-1)} \frac{(l-1)}{(l+j-2)} \cdots \frac{(l+1-m+1)}{(l+j-m+1)},$$

the truncated (to N terms) sum may be written as

$$V_N(l, -m; a, \beta) = \theta_0 \sum_{j=1}^N \theta_j, \quad (\text{A1-2.9})$$

where

$$\theta_0 = \frac{A(l-m+1; a+\beta)}{(l+1)} \left[\frac{a+\beta}{a} \right], \quad (\text{A1-2.9a})$$

$$\theta_1 = \left[\frac{a}{a+\beta} \right] \frac{(l+1)}{(l+1)} \frac{l}{(l+1-1)} \frac{(l-1)}{(l+1-2)} \cdots \frac{(l+1-m+2)}{(l+1-m+2)} \frac{(l+1-m+1)}{(l+1-m+1)} \\ = \left[\frac{a}{a+\beta} \right], \quad (\text{A1-2.9b})$$

$$\theta_2 = \left[\frac{a}{a+\beta} \right]^2 \frac{(l+1)}{(l+2)} \frac{l}{(l+2-1)} \frac{(l-1)}{(l+2-2)} \cdots \frac{(l+1-m+2)}{(l+2-m+2)} \frac{(l+1-m+1)}{(l+2-m+1)} \\ = \left[\frac{a}{a+\beta} \right] \frac{(l+1-m+1)}{(l+2)} \theta_1 = \left[\frac{a}{a+\beta} \right] \frac{(l+2-m)}{(l+2)} \theta_1, \quad (\text{A1-2.9c})$$

and more generally,

$$\theta_j = \left[\frac{a}{a+\beta} \right] \frac{(l+j-m)}{(l+j)} \theta_{j-1}. \quad (\text{A1-2.9d})$$

The resulting algorithm, valid for $l \geq 0$ and $l-m \geq -1$, provides an efficient means of computing the required $V(l, -m; a, \beta)$ integrals with the N-term truncation occurring when the desired accuracy has been met. It differs slightly from the expression given by Öhrn and Nordling due to their extraction of a different multiplicative factor θ_0 , incorporating $A(l-m; a+\beta)/a$, which may not be defined for $l-m = -1$.

Now examine the integral $W(l, m, n; a, \beta, \gamma)$ given in equation (A1-1). Consider first the case where n is non-negative, and apply integration by parts as in (A1-4a) to find

$$\begin{aligned} W(l, m, n; a, \beta, \gamma) &= \sum_{i=0}^n \frac{n!}{i! \gamma^{n+1-i}} \int_0^{\infty} dx x^l e^{-ax} \int_x^{\infty} dy y^{m+i} e^{-(\beta+\gamma)y} \\ &= \sum_{i=0}^n \frac{n!}{i! \gamma^{n+1-i}} V(l, m+i; a, \beta+\gamma). \end{aligned} \quad (\text{A1-1.1})$$

When n is negative, the method of Öhrn and Nordling is used. This is derived in a similar manner to the evaluation of $V(l, -m; a, \beta)$, by starting with the recursion relation

$$W(l, m, n; a, \beta, \gamma) = \frac{1}{l+1} \left\{ a W(l+1, m, n; a, \beta, \gamma) + V(l+m+1, n; a+\beta, \gamma) \right\}, \quad (\text{A1-1.2})$$

valid for $l \geq 0$, $l+m \geq -1$, and $l+m+n \geq -2$, to obtain, for $n < 0$,

$$\begin{aligned} W(l, m, -n; a, \beta, \gamma) &= \sum_{i=1}^M \frac{a^{i-1} l!}{(l+i)!} V(l+i, m, -n; a+\beta, \gamma) \\ &\quad + \frac{a^M l!}{(l+M)!} W(l+M, m, -n; a, \beta, \gamma), \end{aligned} \quad (\text{A1-1.3})$$

For future reference we define the last (remainder) term as

$$R_W(M; l, m, -n; a, \beta, \gamma) = \frac{a^M l!}{(l+M)!} W(l+M, m, -n; a, \beta, \gamma) \quad (A1-1.4)$$

Using equation (A1-2.3) for $V(l+i+m, -n; a+\beta, \gamma)$ in equation (A1-1.3) we obtain

$$\begin{aligned} W(l, m, -n; a, \beta, \gamma) = & \sum_{i=1}^M \frac{a^{i-1} l!}{(l+i)!} \left\{ \sum_{j=1}^k \frac{(a+\beta)^{j-1} (l+i+m)!}{(l+i+m+j)!} A(l+i+m+j-n; a+\beta, \gamma) \right. \\ & \left. + \frac{(a+\beta)^k (l+i+m)!}{(l+i+m+k)!} V(l+i+m+k, -n; a+\beta, \gamma) \right\} \\ & + R_W(M; l, m, -n; a, \beta, \gamma). \end{aligned} \quad (A1-1.5)$$

Setting $k = M-i$,

$$\begin{aligned} W(l, m, -n; a, \beta, \gamma) = & \left\{ V(l+M+m, -n; a+\beta, \gamma) \sum_{i=1}^M \frac{a^{i-1} l!}{(l+i)!} \frac{(a+\beta)^{M-i} (l+i+m)!}{(l+M+m)!} \right\} \\ & + \left[\sum_{i=1}^M \frac{a^{i-1} l!}{(l+i)!} \sum_{j=1}^{M-i} \frac{(a+\beta)^{j-1} (l+i+m)!}{(l+i+m+j)!} A(l+i+m+j-n; a+\beta, \gamma) \right] \\ & + R_W(M; l, m, -n; a, \beta, \gamma) \\ = & \{ A \} + [B] + R_W, \end{aligned} \quad (A1-1.6)$$

with the obvious definitions for A and B. Note that if we set $N = 0$ in equation (A1-2.3) it simply reduces the recursive expression for $V(l, -m; a, \beta)$ to an identity, so that in choosing to set $k = M-i$ in (A1-1.6), it is implied that the sum representing expression B vanishes for $M = 1$.

Let us first examine the expression for the remainder term R_W given in

equation (A1-1.4). An upper bound on this value may be established in a similar manner to the remainder for the integral $V(l, -m; a, \beta)$. Start with

$$\begin{aligned}
 W(l, m, -n; a, \beta, \gamma) &= \int_0^\infty dx x^l e^{-ax} \int_x^\infty dy y^m e^{-\beta y} \int_y^\infty dz z^{-n} e^{-\gamma z} \\
 &= \int_0^\infty dx x^l e^{-ax} \int_x^\infty dy y^{m-n} e^{-\beta y} \int_y^\infty dz \left[\frac{y}{z} \right]^n e^{-\gamma z} \\
 &\leq \int_0^\infty dx x^l e^{-ax} \int_x^\infty dy y^{m-n} e^{-\beta y} \int_y^\infty dz e^{-\gamma z} \\
 &= \frac{1}{\gamma} \int_0^\infty dx x^l e^{-ax} \int_x^\infty dy y^{m-n} e^{-(\beta+\gamma)y} \\
 &= \frac{1}{\gamma} V(l, m-n; a, \beta+\gamma). \tag{A1-1.7}
 \end{aligned}$$

Thus an upper bound on the remainder R_W given by equation (A1-1.4) is

$$R_W(M; l, m, -n; a, \beta, \gamma) \leq \frac{a^M l!}{(l+M)!} \frac{1}{\gamma} V(l+M, m-n; a, \beta+\gamma). \tag{A1-1.4a}$$

When $m-n < 0$, we can use the bound on $V(l, -m; a, \beta)$ given by (A1-2.4) to obtain the upper bound

$$\begin{aligned}
 R_{W, <} &= \frac{a^M l!}{(l+M)!} \frac{1}{\gamma} V(l+M, m-n; a, \beta+\gamma) \\
 &= \frac{a^M l!}{(l+M)!} \frac{1}{\gamma} \frac{1}{\beta+\gamma} A(l+M+m-n; a+\beta+\gamma)
 \end{aligned}$$

$$\begin{aligned}
R_{W,<} &= \frac{a^M l!}{(l+M)!} \frac{1}{\gamma} \frac{1}{\beta+\gamma} \frac{(l+M+m-n)!}{(a+\beta+\gamma)^{l+M+m-n+1}} \\
&= \frac{1}{\gamma} \frac{1}{\beta+\gamma} \frac{a^M l!}{(l+m-n+2)!} \frac{(l+m-n+2)!}{(a+\beta+\gamma)^{l+M+m-n+3}} \frac{(l+M+m-n)!}{(l+M)!} (a+\beta+\gamma)^2 \\
&= \frac{(a+\beta+\gamma)^2}{\gamma(\beta+\gamma)} \left[\frac{a}{a+\beta+\gamma} \right]^M A(l+m-n+2; a+\beta+\gamma) \frac{l!}{(l+m-n+2)!} \frac{(l+M+m-n)!}{(l+M)!} \quad (A1-1.4b)
\end{aligned}$$

When $m-n \geq 0$, a bound on $W(l+M, m, -n; a, \beta, \gamma)$ may be obtained by first placing a bound upon $V(l, m; a, \beta)$ given by (A1-2.1).

$$\begin{aligned}
V(l, m; a, \beta) &= \sum_{j=0}^m \frac{m!}{j!} \frac{1}{\beta^{m+1-j}} A(l+j; a+\beta) \\
&= \sum_{j=0}^m \frac{m!}{j!} \frac{1}{\beta^{m+1-j}} \frac{(l+j)!}{(a+\beta)^{l+j+1}} \\
&= \frac{m!}{\beta^{m+1}} \frac{1}{(a+\beta)^{l+1}} \sum_{j=0}^m \left[\frac{\beta}{a+\beta} \right]^j \frac{(l+j)!}{j!} \\
&\leq \frac{m!}{\beta^{m+1}} \frac{1}{(a+\beta)^{l+1}} \frac{(l+m)!}{m!} \sum_{j=0}^m \left[\frac{\beta}{a+\beta} \right]^j
\end{aligned}$$

The sum over j is a partial sum of terms in a geometric series

$$\sum_{j=0}^m \left[\frac{\beta}{a+\beta} \right]^j = 1 + \sum_{j=1}^m \left[\frac{\beta}{a+\beta} \right]^j = 1 + \frac{\beta}{a} \left\{ 1 - \left[\frac{\beta}{a+\beta} \right]^m \right\}$$

Dropping the term involving m in the last expression,

$$\sum_{j=0}^m \left[\frac{\beta}{a+\beta} \right]^j \leq 1 + \frac{\beta}{a} = \frac{a+\beta}{\beta},$$

so the bound on $V(l, m; a, \beta)$ is given by

$$V(l, m; a, \beta) \leq \frac{1}{\beta^{m+1}} \frac{l!}{(a+\beta)^{l+1}} \frac{(l+m)!}{l!} \frac{a+\beta}{\beta} = \frac{a+\beta}{\beta^{m+2}} \frac{(l+m)!}{l!} A(l; a+\beta) \quad (\text{A1-2.4a})$$

Using this result, an upper bound upon the remainder R_W when $m-n \geq 0$ is

$$\begin{aligned} R_{W, \geq} &= \frac{a^M l!}{(l+M)!} \frac{1}{\gamma} \frac{a+\beta+\gamma}{\beta^{m-n+2}} \frac{(l+M+m-n)!}{(l+M)!} A(l+M; a+\beta+\gamma) \\ &= \frac{a^M l!}{(l+M)!} \frac{1}{\gamma} \frac{a+\beta+\gamma}{\beta^{m-n+2}} \frac{(l+M+m-n)!}{(l+M)!} \frac{(l+M)!}{(a+\beta+\gamma)^{l+M+1}} \\ &= \frac{1}{\gamma} \frac{a+\beta+\gamma}{\beta^{m-n+2}} \frac{l!}{(a+\beta+\gamma)^{l+1}} \frac{(l+M+m-n)!}{(l+M)!} \left[\frac{a}{a+\beta+\gamma} \right]^M \\ &= \frac{1}{\gamma} \frac{a+\beta+\gamma}{\beta^{m-n+2}} A(l; a+\beta+\gamma) \frac{(l+M+m-n)!}{(l+M)!} \left[\frac{a}{a+\beta+\gamma} \right]^M \quad (\text{A1-1.4c}) \end{aligned}$$

Note that bounds $R_{W, <}$ and $R_{W, \geq}$ are proportional to one another and display the same dependence upon M . Each subsequent increase in the value of M reduces the bounds by a factor

$$\frac{(l+M+m-n)}{(l+M)} \left[\frac{a}{a+\beta+\gamma} \right],$$

which tends to

$$1 \times \left[\frac{a}{a+\beta+\gamma} \right]$$

as M becomes very large, so subsequent terms are reduced almost geometrically.

Now examine expression A of equation (A1-1.6).

$$A = V(l+M+m, -n; a+\beta, \gamma) \sum_{i=1}^M \frac{a^{i-1} l!}{(l+i)!} \frac{(a+\beta)^{M-i} (l+i+m)!}{(l+M+m)!}$$

Expanding the integral V again using equation (A1-2.3),

$$\begin{aligned} A = & \left\{ \sum_{j=1}^N \frac{(a+\beta)^{j-1} (l+M+m)!}{(l+M+m+j)!} A(l+M+m+j-n; a+\beta, \gamma) \right. \\ & \left. + \frac{(a+\beta)^N (l+M+m)!}{(l+M+m+N)!} V(l+M+m+N, -n; a+\beta, \gamma) \right\} \\ & \times \frac{(a+\beta)^M}{a} \frac{l!}{(l+M+m)!} \sum_{i=1}^M \left[\frac{a}{a+\beta} \right]^i \frac{(l+i+m)!}{(l+i)!} \quad (\text{A1-1.8a}) \end{aligned}$$

The sum over M may be written in terms of the auxiliary function

$$X(l, m, M; r) \doteq \sum_{i=1}^M x_i(l, m; r) = \sum_{i=1}^M r^i \frac{(l+i+m)!}{(l+i)!} \quad (\text{A1-4a})$$

$$\text{where} \quad x_1(l, m; r) = r \frac{(l+m+1)!}{(l+1)!} \quad (\text{A1-4b})$$

and
$$x_i(l, m; r) = r \frac{(l+m+i)}{(l+i)} x_{i-1}, \quad i > 1 \quad (\text{A1-4b})$$

Expression A may be written using this form for the sum over M as

$$\begin{aligned} A &= \left\{ \frac{(a+\beta)^M}{a} \frac{l!}{(l+M+m)!} X(l, m, M; \frac{a}{a+\beta}) \right. \\ &\quad \times \sum_{j=1}^N \frac{(a+\beta)^{j-1} (l+M+m)!}{(l+M+m+j)!} A(l+M+m+j-n; a+\beta+\gamma) \Big\} \\ &+ \left[\frac{(a+\beta)^{M+N}}{a} \frac{l!}{(l+M+m+N)!} X(l, m, M; \frac{a}{a+\beta}) V(l+M+m+N, -n; a+\beta, \gamma) \right] \\ &= \{ A(M, N) \} + [R_A(M, N)] \quad (\text{A1-1.8b}) \end{aligned}$$

with the obvious definitions for $A(M, N)$ and $R_A(M, N)$. By explicitly representing the value of the A integral, $A(M, N)$ may be expressed as a product of two X functions:

$$\begin{aligned} A(M, N) &= \frac{(a+\beta)^{M-1}}{a} l! X(l, m, M; \frac{a}{a+\beta}) \\ &\quad \times \sum_{j=1}^N \frac{(a+\beta)^j}{(l+M+m+j)!} \frac{(l+M+m+j-n)!}{(a+\beta+\gamma)^{l+M+m+j-n+1}} \\ &= \frac{(a+\beta)^{M-1}}{a(a+\beta+\gamma)} \frac{l!}{l+M+m-n+1} X(l, m, M; \frac{a}{a+\beta}) \\ &\quad \times \sum_{j=1}^N \left[\frac{a+\beta}{a+\beta+\gamma} \right]^j \frac{(l+M+m+j-n)!}{(l+M+m+j)!} \\ &= \frac{1}{a} \left[\frac{a+\beta}{a+\beta+\gamma} \right]^{M-1} \frac{l!}{(a+\beta+\gamma)^{l+m-n+2}} X(l, m, M; \frac{a}{a+\beta}) \\ &\quad \times X(l+M+m, -n, N; \frac{a+\beta}{a+\beta+\gamma}) \end{aligned}$$

$$A(M,N) = \frac{1}{a} \left[\frac{a+\beta}{a+\beta+\gamma} \right]^{M-1} \frac{l!}{(l+m-n+1)!} A(l+m-n+1; a+\beta+\gamma) \\ \times X(l,m,M; \frac{a}{a+\beta}) X(l+M+m, -n, N; \frac{a+\beta}{a+\beta+\gamma})$$

However, the only condition on l , m and n is that $l+m-n \geq -2$, so the factorial and the integral A are not necessarily defined. Therefore we rewrite the above as

$$A(M,N) = \left[\frac{a+\beta+\gamma}{a} \right] \left[\frac{a+\beta}{a+\beta+\gamma} \right]^{M-1} \frac{l!}{(l+m-n+2)!} A(l+m-n+2; a+\beta+\gamma) \\ \times X(l,m,M; \frac{a}{a+\beta}) X(l+M+m, -n, N; \frac{a+\beta}{a+\beta+\gamma}) \quad (A1-1.9a)$$

This may be reorganized slightly for ease of comparison with the work of Öhrn and Nordling as

$$A(M,N) = \frac{A(l+m-n+2; a+\beta+\gamma)}{(l+1)} \left[\frac{a+\beta}{a+\beta+\gamma} \right]^{M-1} \frac{(l+1)!}{(l+m-n+2)!} \left[\frac{a+\beta+\gamma}{a} \right] \\ \times X(l+M+m, -n, N; \frac{a+\beta}{a+\beta+\gamma}) X(l,m,M; \frac{a}{a+\beta}). \quad (ON-1)$$

Note that we could redefine the starting point of the recursion formula for $X(l,m,M;r)$ if $l+m \geq 0$ (which is not always the case for the recursion formula given in equation (A1-1.2)) by taking a factor of $(l+m)!/l!$ out of the series, i.e., let

$$X(l,m,M;r) = \frac{(l+m)!}{l!} X'(l,m,M;r) = \frac{(l+m)!}{l!} \sum_{i=1}^M x'_i(l,m;r) \quad (ON-2a)$$

$$\text{where} \quad x'_0(l,m;r) = 1 \quad (ON-2b)$$

$$\text{and} \quad x'_i(l,m;r) = r \frac{(l+m+i)}{(l+i)} x'_{i-1}, \quad i > 1 \quad (ON-2c)$$

Using this expression for the series represented by the function X , $A(M,N)$ is given by

$$\begin{aligned}
 A(M,N) &= \frac{A(l+m-n+2; a+\beta+\gamma)}{(l+1)} \left[\frac{a+\beta}{a+\beta+\gamma} \right]^{M-1} \frac{(l+1)!}{(l+m-n+2)!} \left[\frac{a+\beta+\gamma}{a} \right] \\
 &\times \frac{(l+M+m-n)!}{(l+M+m)!} \frac{(l+m)!}{l!} X'(l+M+m, -n, N; \frac{a+\beta}{a+\beta+\gamma}) X'(l, m, M; \frac{a}{a+\beta}) \\
 &= \frac{(l+m)!}{l!} \left\langle \frac{A(l+m-n+1; a+\beta+\gamma)}{(l+1) (a+\beta+\gamma)} \right\rangle \\
 &\times \left\{ \left[\frac{a+\beta}{a+\beta+\gamma} \right]^{M-1} \frac{(l+1)!}{(l+m-n+1)!} \frac{(l+M+m-n)!}{(l+M+m)!} \left[\frac{a+\beta+\gamma}{a} \right] \right. \\
 &\quad \left. \times X'(l+M+m, -n, N; \frac{a+\beta}{a+\beta+\gamma}) \right\} X'(l, m, M; \frac{a}{a+\beta}) \\
 &= \frac{(l+m)!}{l!} \langle W_0 \rangle \{ X_0 \} X'(l, m, M; \frac{a}{a+\beta}), \quad (\text{ON-3})
 \end{aligned}$$

where the implicit definitions of the quantities W_0 and X_0 in the last line are consistent with the definitions used by Öhrn and Nordling in their equation (30), and $X'(l, m, M; \frac{a}{a+\beta})$ represents the first sum in that equation. The expression for $A(M,N)$ given above differs, however, from the value of the corresponding (first) term in equation (30) by the factor $(l+m)!/l!$, which is missing from their expression. Note also that the quantity X_0 vanishes for M infinite. Öhrn and Nordling use this as the basis for a very useful approximation scheme (their equation (33)) in which $A(M,N)$ is omitted entirely from the calculation of $W(l, m, -n; a, \beta, \gamma)$.

As the recursion relation given in equation (A1-1.2) is only valid for $l+m \geq -1$ and $l+m-n \geq -2$, to allow for the equalities we avoid the use of the X' form of the

series given in (ON-2a)-(ON-2c) and also the use of $A(l+m-n+1; a, \beta, \gamma)$. Thus the expression corresponding to (ON-3) is

$$\begin{aligned}
 A(M, N) &= \frac{(l+m)!}{l!} \left\langle \frac{A(l+m-n+2; a+\beta+\gamma)}{(l+1)} \right\rangle \\
 &\times \left\{ \left[\frac{a+\beta}{a+\beta+\gamma} \right]^{M-1} \frac{(l+1)!}{(l+m-n+2)!} \left[\frac{a+\beta+\gamma}{a} \right] X(l+M+m, -n, N; \frac{a+\beta}{a+\beta+\gamma}) \right\} \\
 X(l, m, M; \frac{a}{a+\beta}) \\
 &= \frac{(l+m)!}{l!} \langle W_1 \rangle \{ X_1 \} X(l, m, M; \frac{a}{a+\beta}), \quad (A1-1.9b)
 \end{aligned}$$

Turn next to the term $R_A(M, N)$ in equation (A1-1.8b). An upper bound upon $R_A(M, N)$ may be found using the bound for the integral V given in equation (A1-2.4) once a similar bound is obtained for the function X defined in (A1-4a). The latter is developed in similar fashion to the bound given in (A1-2.4a), by extracting the largest ratio of factorials in the sum and retaining only the most significant part of the expression for the sum of the first M terms in the remaining geometric series:

$$\begin{aligned}
 X(l, m, M; \frac{a}{a+\beta}) &= \sum_{i=1}^M \left[\frac{a}{a+\beta} \right]^i \frac{(l+i+m)!}{(l+i)!} \\
 &< c_m \sum_{i=1}^M \left[\frac{a}{a+\beta} \right]^i = c_m \frac{a}{\beta} \left\{ 1 - \left[\frac{a}{a+\beta} \right]^M \right\} < c_m \frac{a}{\beta},
 \end{aligned}$$

where

$$\begin{aligned}
 c_m &= \frac{(l+M+m)!}{(l+M)!} \quad \text{for } m \geq 0, \text{ and} \\
 &= \frac{(l+1+m)!}{(l+1)!} \quad \text{for } m < 0.
 \end{aligned}$$

The resulting upper bound upon the value of $R_A(M, N)$ is then

$$\begin{aligned}
 R_A(M, N) &= \frac{(a+\beta)^{M+N}}{a} \frac{l!}{(l+M+m+N)!} X(l, m, M; \frac{a}{a+\beta}) V(l+M+m+N, -n; a+\beta, \gamma) \\
 &< \frac{(a+\beta)^{M+N}}{a} \frac{l!}{(l+M+m+N)!} c_m \frac{a}{\beta} V(l+M+m+N, -n; a+\beta, \gamma) \\
 &< \frac{(a+\beta)^{M+N}}{a} \frac{l!}{(l+M+m+N)!} c_m \frac{a}{\beta} \frac{1}{\gamma} \frac{(l+M+m+N-n)!}{(a+\beta+\gamma)^{l+M+m+N-n+1}} \\
 &< c_m \frac{1}{\beta \gamma} \frac{l!}{(a+\beta+\gamma)^{l+m-n+1}} \frac{(l+M+m+N-n)!}{(l+M+m+N)!} \left[\frac{a+\beta}{a+\beta+\gamma} \right]^{M+N} \quad (A1-1.8c)
 \end{aligned}$$

As with the remainder $R_W(M)$, this term can be made as small as we wish by choosing M and/or N sufficiently large.

Now we examine expression B from equation (A1-1.6).

$$\begin{aligned}
 B &= \sum_{i=1}^M \frac{a^{i-1} l!}{(l+i)!} \sum_{j=1}^{M-i} \frac{(a+\beta)^{j-1} (l+i+m)!}{(l+i+m+j)!} A(l+i+m+j-n; a+\beta+\gamma) \\
 &= \sum_{i=1}^M \frac{a^{i-1} l!}{(l+i)!} \sum_{j=1}^{M-i} \frac{(a+\beta)^{j-1} (l+i+m)!}{(l+i+m+j)!} \frac{(l+m-n+i+j)!}{(a+\beta+\gamma)^{l+m-n+i+j+1}} \\
 &= \frac{(l+m-n+2)!}{(a+\beta+\gamma)^{l+m-n+3}} \sum_{i=1}^M \frac{a^{i-1} l!}{(l+i)!} \sum_{j=1}^{M-i} \frac{(a+\beta)^{j-1} (l+i+m)!}{(l+i+m+j)!} \\
 &\quad \times \frac{(l+m-n+i+j)!}{(l+m-n+2)!} \frac{1}{(a+\beta+\gamma)^{i+j-2}}
 \end{aligned}$$

$$\begin{aligned}
B &= A(l+m-n+2; a+\beta+\gamma) \sum_{i=1}^M \left[\frac{a}{a+\beta+\gamma} \right]^{i-1} \frac{l!}{(l+i)!} \\
&\quad \times \sum_{j=1}^{M-i} \left[\frac{a+\beta}{a+\beta+\gamma} \right]^{j-1} \frac{(l+i+m)!}{(l+i+m+j)!} \frac{(l+m-n+i+j)!}{(l+m-n+2)!} \\
&= A(l+m-n+2; a+\beta+\gamma) \frac{l!}{(l+m-n+2)!} \sum_{i=1}^M \left[\frac{a}{a+\beta+\gamma} \right]^{i-1} \frac{(l+i+m)!}{(l+i)!} \\
&\quad \times \sum_{j=1}^{M-i} \left[\frac{a+\beta}{a+\beta+\gamma} \right]^{j-1} \frac{(l+m-n+i+j)!}{(l+i+m+j)!} \quad (\text{A1-1.10a})
\end{aligned}$$

Letting $r = \frac{a}{a+\beta+\gamma}$ and $R = \frac{a+\beta}{a+\beta+\gamma}$, we can write

$$B = A(l+m-n+2; a+\beta+\gamma) \frac{l!}{(l+m-n+2)!} \sum_{i=1}^M y_i \quad (\text{A1-1.10b})$$

where
$$y_i = r^{i-1} \frac{(l+i+m)!}{(l+i)!} \sum_{j=1}^{M-i} R^{j-1} \frac{(l+m-n+i+j)!}{(l+i+m+j)!}.$$

With some effort this sum over i may be transformed into a more convenient form for recursive calculation, i.e.

$$\sum_{i=1}^M y_i = \sum_{i=2}^M z_i, \quad (\text{A1-1.11})$$

where

$$z_i = \frac{(l+m-n+i)!}{(l+m+i)!} \sum_{j=2}^i R^{j-2} r^{i-j} \frac{(l+m-n+i+j)!}{(l+i+m+j)!} \quad (\text{A1-1.11a})$$

may be obtained from the recursion relations

$$z_i = \frac{(l+m-n+i)!}{(l+m+i)!} [a_{i-1} + R z_{i-1}] \quad \text{for } i \geq 2 \quad (\text{A1-1.11b})$$

with $z_1 \doteq 0$ and a_i determined also by recursion according to the relation

$$a_i = \frac{(l+m-n+i)!}{(l+i)!} r a_{i-1} \quad \text{for } i \geq 2 \quad (\text{A1-1.11c})$$

with

$$a_1 = \frac{(l+m-n+1)!}{(l+1)!}. \quad (\text{A1-1.11d})$$

If this common factor is removed, redefining the starting point for the recursion as $a_1' = 1$ with the corresponding changes to the values z_i , which are denoted z_i' , we can write

$$\begin{aligned} B &= A(l+m-n+2; a+\beta+\gamma) \frac{l!}{(l+m-n+2)!} \frac{(l+m-n+1)!}{(l+1)!} \sum_{i=2}^M z_i' \\ &= \frac{A(l+m-n+1; a+\beta+\gamma)}{(l+1)! (a+\beta+\gamma)} \sum_{i=2}^M z_i' = W_0 \sum_{i=2}^M z_i', \quad (\text{ON-4}) \end{aligned}$$

which is the Öhrn and Nordling result. As before, to allow for the case where $l+m-n = -2$, we start the recursion one step higher, i.e., we still use

$$z_i = \frac{(l+m-n+i)!}{(l+m+i)!} [a_{i-1} + R z_{i-1}], \quad \text{but for } i \geq 3, \quad (\text{A1-1.12})$$

with

$$z_2 = \frac{(l+m-n+2)!}{(l+m+2)(l+1)!},$$

$$a_2 = \frac{(l+m-n+2)!}{(l+2)!} r, \quad \text{and} \quad a_i = \frac{(l+m-n+i)}{(l+i)} r a_{i-1} \quad \text{for } i \geq 3.$$

Then, extracting a common factor of $(l+m-n+2)!/(l+1)!$ we redefine these starting from

$$z''_2 = \frac{1}{(l+m+2)} \quad \text{and} \quad a''_2 = \frac{1}{(l+2)!} r, \quad (\text{A1-1.13})$$

to obtain the following expression for B:

$$\begin{aligned} B &= A(l+m-n+2; a+\beta+\gamma) \frac{l!}{(l+m-n+2)!} \frac{(l+m-n+2)!}{(l+1)!} \sum_{i=3}^M z''_i \\ &:= \frac{A(l+m-n+2; a+\beta+\gamma)}{(l+1)} \sum_{i=3}^M z''_i = W_1 \sum_{i=3}^M z''_i. \end{aligned} \quad (\text{A1-1.14})$$

Thus in analogy with equation (30) of Öhrn and Nordling, our final expression for $W(l, m, -n; a, \beta, \gamma)$ is

$$\begin{aligned} W(l, m, -n; a, \beta, \gamma) &= A(M, N) + B(M) + R_W(M) + R_A(M, N) \\ &= W_1 X_1 X(l, m, M; \frac{a}{a+\beta}) + W_1 \sum_{i=2}^M z''_i + R_W(M) + R_A(M, N) \end{aligned} \quad (\text{A1-1.15})$$

where W_1 and X_1 are defined via equation (A1-1.9b), $X(l, m, M; \frac{a}{a+\beta})$ is given by equations (A1-4a) - (A1-4c), $R_W(M; l, m, -n; a, \beta, \gamma)$ is given by (A1-1.4) and the

recursion relations for the z'' series in $B(M)$ are given by (A1-1.12) and (A1-1.13). The approximation corresponding to equation (33) of Öhrn and Nordling, which retains only expression $B(M)$ above, has been used in the calculations in this study.

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